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Rate and Oxygen Activity Oscillations during Hydrogen Oxidation on Polycrystalline Nickel

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The catalytic oxidation of hydrogen on polycrystalline nickel films supported on yttria stabilized zirconia was studied in a continuous flow reactor at temperatures between 280 and 400°C and atmospheric total pressure. The technique of solid electrolyte potentiometry (SEP) was used to monitor the thermodynamic activity of oxygen adsorbed on the catalyst surface. The limits of gas phase composition and temperature within which sustained oscillations appear were investigated. It was found that the boundaries within which unsteady state phenomena occur depend upon the catalyst temperature and the partial pressures of both reactants, hydrogen and oxygen. The minimum surface oxygen activity below which only stable steady states are observed is very close to the dissociation pressure of nickel oxide.

INTRODUCTION

The hydrogen–oxygen reaction appears to be one of the simplest to study and of no significant technological interest since the product, water, is in abundant supply. The reaction is, however, of great technological relevance through its connection with new technologies (*1, 2*) developed to make hydrogen an important energy "currency" in the future. On the other hand, the hydrogen–oxygen recombination on metal surfaces is not as simple as expected and considerable differences are observed on various catalysts.

The catalytic oxidation of H_2 on nickel has been studied since the beginning of the century by a large number of investigators but no generally accepted mechanism has been established (*1, 3–6*). Moreover, in 1973 Belyaev *et al.* (*7*) first reported that under certain conditions the reaction exhibits self-sustained oscillations. Oscillatory behavior in heterogeneous catalytic reactions has attracted considerable attention in the last 15 years and the subject has been reviewed by a number of workers (*8–10*). Several theoretical models have been developed to explain these phenomena (*11–16*) but a gap still exists between experimental observations and the theoretical models proposed.

The observations of Belyaev *et al.* were substantiated and further investigated by a number of workers (*17–23*). Schmitz *et al.* (*17*) observed nonisothermal oscillations on a Ni foil when the feed temperature was between 230 and 250°C and the feed oxygen concentration was kept below 5%. Schmitz *et al.* measured temperature changes only and they suggested that *in situ* surface techniques could add important information on the mechanism of the oscillations and the relative influence of adsorption, surface reaction, and transport phenomena. Later Kurtanjek *et al.* studied in detail the above reaction on nickel plate at temperatures between 160 and 400°C in a continuous flow reactor (*18, 19*). The above investigators simultaneously measured the kinetic and contact potential difference (CPD) behavior. Their work showed that (a) oscillations appear when mixtures of large excess of hydrogen are introduced into the reactor and (b) the oscillations are simple for appreciable mass transfer resis-

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tances and aperiodic (chaotic) when the mass and heat transfer resistances are small. In the latter case temperature oscillations on the surface are of negligible amplitude (less than 0.5°C). Also, (c) the dynamic behavior of the system is sensitive to the pretreatment of the surface.

According to the above work, the observed unsteady phenomena are related to periodic oxidation and reduction of the nickel surface. Based on this hypothesis Kurtanjek later proposed a kinetic model that provided reasonable agreement with the experimental observations (*22*). Similar kinetic models based on periodic oxidation and reduction of the catalyst have been proposed to explain oscillatory phenomena observed during ethylene oxidation (*14*) and CO oxidation (*23*) over platinum surfaces.

In a recent study kinetics were combined with simultaneous *in situ* measurement of the thermodynamic activity of oxygen adsorbed on the nickel surface (*21*). A brief summary of the results of that work is included under Results.

The purpose of the present communication is to report a number of kinetic and potentiometric observations obtained during a period of more than 2 years in our laboratory (*24–26*). We will also attempt to compare our results with the work of previous investigators.

EXPERIMENTAL

The experimental apparatus has been described in detail in a previous communication (*21*). The basic principle of solid electrolyte potentiometry (SEP) that was used for the continuous measurement of the surface oxygen activity has also been described previously (*21, 27, 28*). The above technique utilizes an 8% yttria stabilized zirconia solid electrolyte cell with one of the electrodes exposed to the reacting mixture and thus serving as a catalyst for the reaction under study. The other electrode is exposed to the ambient air and serves as the reference electrode. The two electrodes are connected by a differential voltmeter and under open-circuit operation the thermodynamic activity α_0 of atomic oxygen adsorbed on the catalyst surface is given by

$$\alpha_0 = (0.21)^{1/2} \exp(2FE/RT) \qquad (1)$$

where F is the Faraday constant, R is the ideal gas constant, T is the absolute temperature, and E is the electromotive force of the cell.

The polycrystalline porous nickel film catalyst preparation and characterization has also been described previously (*21*). Silver instead of nickel was used as reference electrode mainly because silver adheres to the zirconia wall much more strongly than nickel. The silver electrode preparation procedure has been described elsewhere (*28*).

Additional information about the experimental apparatus and procedure can be found in Refs. (*21, 24–26*).

RESULTS

General

The reaction rate and the oxygen activity behavior was studied at temperatures between 280 and 400°C and atmospheric total pressure. Under the flowrates employed the reactor could be considered completely mixed (*21, 24*). The oxygen partial pressure in the reactor varied between zero and 0.12 bar and that of hydrogen between zero and 0.25 bar. Nitrogen or helium was used as the diluent. Due to catalyst deactivation several reactor cells had to be prepared. Each reactor cell contained 110 mg nickel and the catalyst preparation was identical for all of them.

The nickel catalyst film was prepared using Engelhard 58-A nickel resinate. A few drops of the resinate solution were applied to the zirconia surface followed by drying and heating at 400°C for 2–3 h. The catalyst was then subjected to several cycles of oxidation and reduction. The surface was assumed to be ready for experiment after reproducible voltage readings were obtained in successive oxidation–reduction cycles. After the end of each experiment the catalyst was heated to 400°C and reduced in a hydrogen stream for 8–10 h. Following the above procedure which was first adopted by Kurtanjek *et al.* (*18*) we were able to obtain reproducible results over a period of several weeks. A newly prepared catalyst was subjected to a "control" test. This test consisted in measuring the reaction rate and the EMF of the cell at 400°C with outlet P_{H_2} and P_{O_2} kept at 0.037 and 0.08 bar, respectively. The test was repeated every 7–10 days and whenever the measured EMF or reaction rate deviated more than 10% from its original value a new reactor cell was prepared. The usual lifetime for a cell was 3–4 weeks. Hence a large number of reactor cells was prepared. Nevertheless each reactor contained the same amount of nickel and in most cases the control test gave the same rate and α_0 values for any new catalyst.

The effect of homogeneous gas-phase oxidation of hydrogen has been reported in a previous communication (*21*). The homogeneous rate was negligible at temperatures lower than 330°C and could come up to 6–7% of the catalytic reaction rate at 400°C. Thus only the kinetic results obtained at 400°C were corrected by subtracting the homogeneous effect.

Unless specifically mentioned for some particular experiments, intrapellet as well as external diffusion problems were eliminated (*21*). Temperature oscillations were very small under these conditions. The reading of the thermocouple attached to the catalyst surface did not vary by more than 1–1.5°C while the rate and EMF were fluctuating by 30% or more from an average value. We called these oscillations "isothermal" to distinguish from cases where due to diffusional effects the surface temperature oscillated by 20°C or more.

Typical examples of the EMF and the outlet P_{O_2} behavior vs time are shown in Fig. 1 for P_{O_2} = 0.013 bar and T = 400°C. The last two experiments (c and d) were nonisothermal and the effect of diffusional limitations was strong. The temperature at

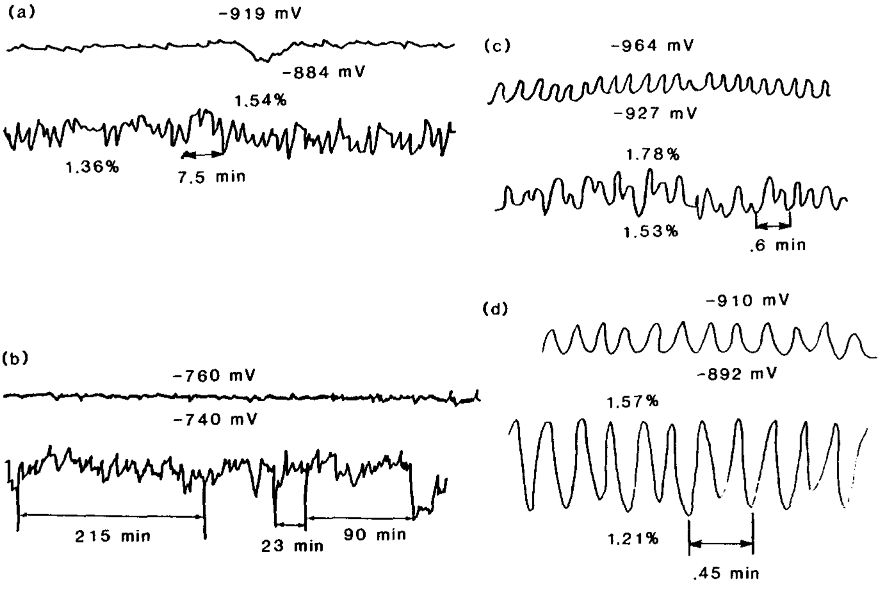

FIG. 1. Kinetic and SEP measurements at 400°C and P_{O_2} = 0.013 bar. (a) $P_{H_2} \simeq 0.14$ bar, (b) $P_{H_2} \simeq$ 0.048 bar, (c) $P_{H_2} \simeq 0.51$ bar, (d) $P_{H_2} \simeq 0.88$ bar.

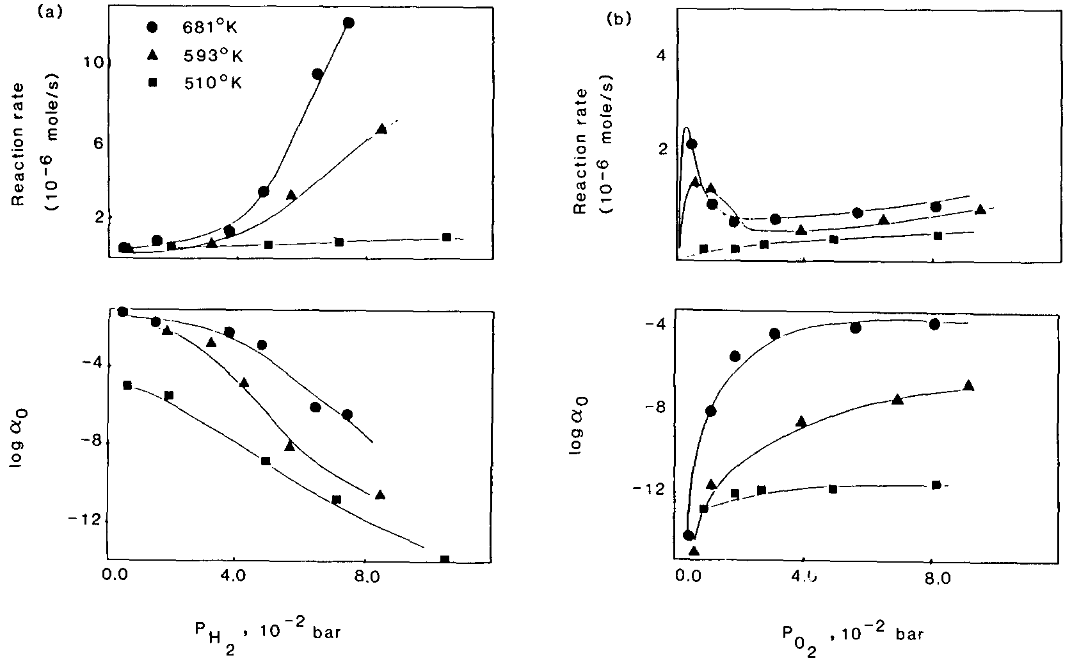

FIG. 2. Stable steady state kinetic and SEP results: (a) effect of P_{H_2} (P_{O_2} = 0.05 bar); (b) effect of P_{O_2} (P_{H_2} = 0.018 bar).

the surface varied from 344 to 369°C in case c and from 346 to 368° in case d. Note that when the system becomes nonisothermal the oscillations become periodic and the period decreases drastically. The surface oxygen activity and the reaction rate oscillate simultaneously and in general an increase in the reaction rate (decrease in outlet P_{O_2}) is accompanied by a decrease in α_0 (increase in EMF).

Summary of Previous Stable Steady State Results

It would be useful before we present the results of this work to summarize briefly the work that has already been published (*21*) since both studies involved the same apparatus and experimental methods, identical catalyst preparation, and similar temperature and gas composition. The results of the previous work are:

(1) For constant outlet P_{O_2} and temperature the reaction rate increases slowly with increasing P_{H_2} until $P_{H_2}/P_{O_2} = 1$. Above this ratio the rate dependence on P_{H_2} becomes more pronounced so that the apparent order of reaction is higher than one with respect to H_2. This behavior is not observed at the lowest temperature examined (Fig. 2a).

(2) For constant temperature and outlet P_{H_2} the rate increases sharply with P_{O_2}, reaches a maximum, and then decreases drastically. For even higher P_{O_2} the rate becomes almost independent of P_{O_2} (Fig. 2b). Again this peculiar behavior is not observed at temperatures lower than 280°C.

(3) The surface oxygen activity attains extremely low values for large P_{H_2}/P_{O_2} (Fig. 2b) and therefore α_0 can be 10 orders of magnitude lower than the values predicted assuming thermodynamic equilibrium between gaseous and adsorbed oxygen. This observation indicates that the rates of oxygen adsorption and surface reaction attain comparable values under these conditions.

The above experiments were done under such conditions that both the reaction rate and the surface oxygen activity exhibited stable steady states. Nitrogen was used as a diluent.

Effect of Diluent

Kurtanjek *et al.* (*18*) noticed that when the nitrogen concentration exceeded 40 vol% in the reactor the limits of O_2 concentration within which oscillations occur were shifted to higher values of P_{O_2}. Furthermore the frequency of oscillations and the CPD values were affected at these high N_2 concentrations.

We conducted experiments using either nitrogen or helium as a diluent. We did not observe notable differences in the behavior of the system by changing from one diluent to the other even at nitrogen concentrations as high as 85 vol%. Furthermore we conducted the following experiments:

Using nitrogen as diluent the reactor was set at a desired temperature and the outlet P_{O_2} and P_{H_2}, the reaction rate, and the open-circuit EMF of the cell were measured. Then a helium stream replaced nitrogen while the outlet P_{O_2} and P_{H_2} were maintained constant. The reaction rate and the SEP value were measured again. Similar experiments were conducted using helium at the beginning and replacing it with nitrogen.

Results are shown in Fig. 3 where the rate and α_0 measured with N_2 and with He as diluent are compared. It can be seen that the behavior of the reaction system is not affected by replacing He with N_2 or vice versa.

Transition Concentrations

All experiments described in this section were obtained as follows. The catalyst surface was exposed overnight to a hydrogen stream at 400°C. Hence starting with a reduced catalyst, the temperature and the H_2, O_2, and He flowmeters were set at the desired level. A number of experiments were then completed with the outlet concentration of either reactant kept constant. This required an a priori estimation of the reaction rate. In cases where the rate oscillated this constant outlet P_{O_2} or P_{H_2} referred to an average value which in most cases did not differ more than ±15% from the minimum or maximum values obtained. Although more difficult this procedure was more meaningful because the conversion with respect to oxygen could vary from 10 to 80% and hence the inlet concentrations were inappropriate to use in rate and α_0 correlations.

Figures 4–7 refer to experiments con-

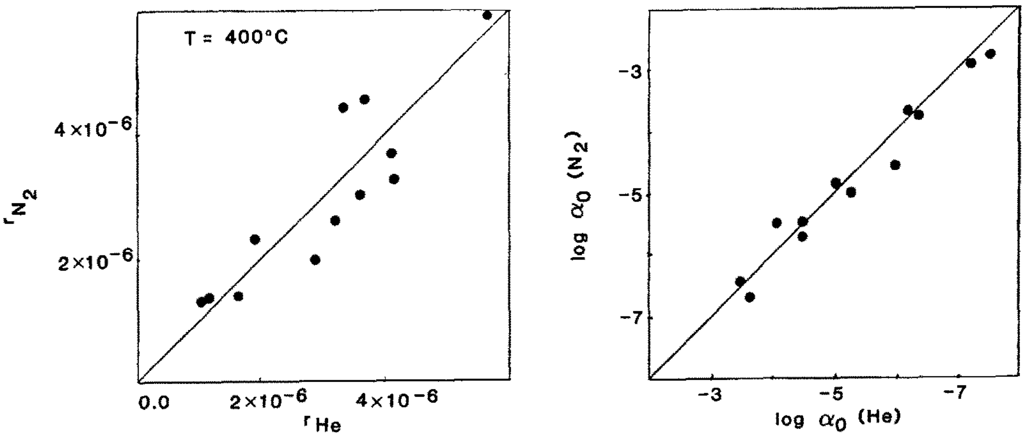

FIG. 3. Effect of diluent gas on rate and SEP behavior: r_{N_2}, α_0 (N_2), rate and oxygen activity measured with nitrogen as diluent; r_{He}, α_0 (He), rate and oxygen activity measured with helium as diluent.

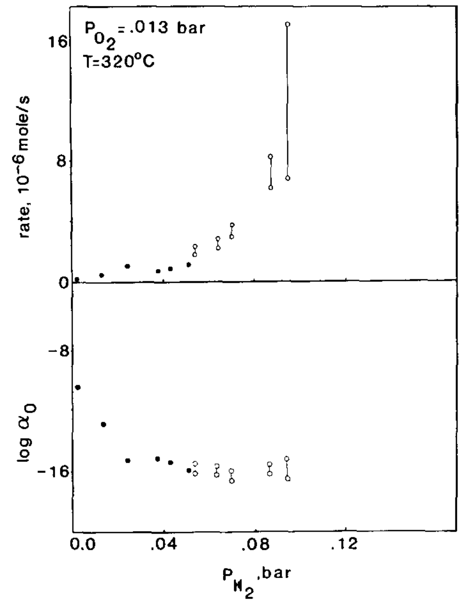

FIG. 4. Effect of P_{H_2} on rate and α_0; T = 320°C, $P_{O_2} \simeq 0.013$ bar.

ducted at 320°C. Figure 4 contains data for outlet P_{O_2} = 0.013 bar and P_{H_2} varying from zero to 0.10 bar. The top portion contains the kinetic measurements and the bottom portion contains the corresponding α_0 measurements. For outlet P_{H_2} lower than 0.05 bar, stable steady states are obtained. Oscillations appear at $P_{H_2} \simeq 0.053$ bar. The filled circles correspond to stable steady states and the open circles connected with a vertical line correspond to the highest and lowest values of rate and α_0 of the oscillatory states. A similar curve is shown in Fig. 5 for outlet $P_{O_2} \simeq 0.05$ bar. Stable steady states are obtained in this case for P_{H_2} as high as 0.095 bar. Figures 6 and 7 show the rate and α_0 dependence on P_{O_2} for P_{H_2} kept at 0.018 and 0.040, respectively. The oscillatory regime is in all cases bound by two stable steady state regions. Nevertheless the points of transition from stable to oscillatory state depend on the partial pressure of hydrogen in the reactor.

Similar results have been obtained at temperatures of 400, 360, and 280°C (*25*).

Hysteresis Phenomena

The measurements shown in Fig. 8 were obtained with a catalyst treatment different from that described in the previous section.

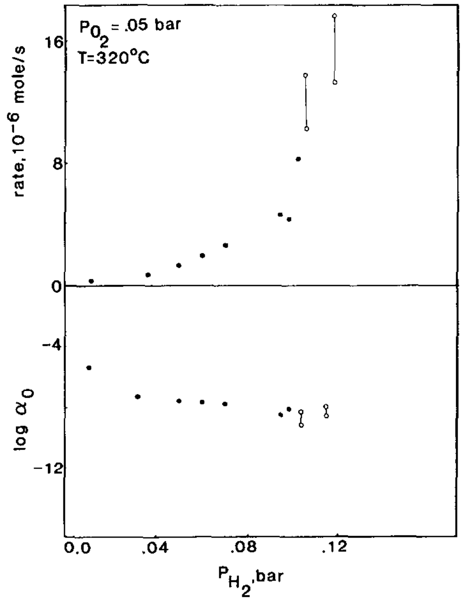

FIG. 5. Effect of P_{H_2} on rate and α_0; T = 320°C, $P_{O_2} \simeq 0.05$ bar.

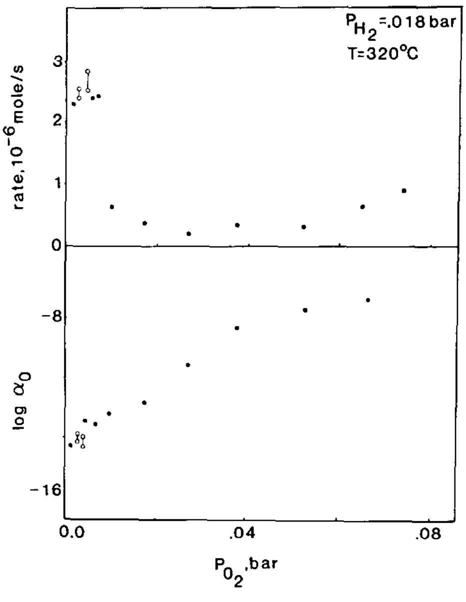

FIG. 6. Effect of P_{O_2} on rate and α_0; T = 320°C, P_{H_2} = 0.018 bar.

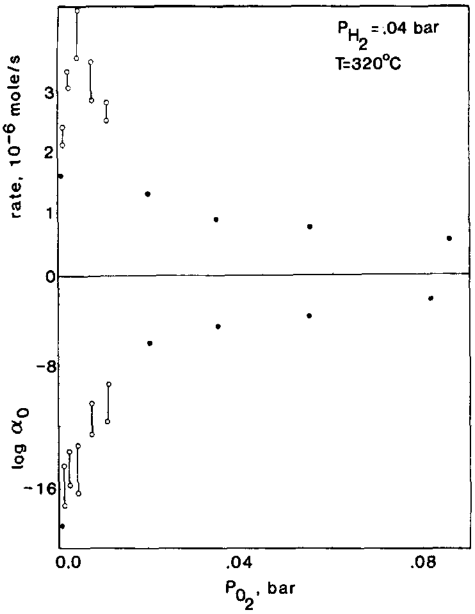

FIG. 7. Effect of P_{O_2} on rate and α_0; T = 320°C, P_{H_2} = 0.04 bar.

Starting with a reduced surface the oxygen concentration was gradually increased while the temperature and outlet P_{H_2} were maintained at 320°C and 0.04 bar, respectively. The filled circles correspond to a gradual increase in P_{O_2} from zero to 0.085 bar. The open circles correspond to data obtained by decreasing P_{O_2} from 0.085 to 0.002 bar. The surface was not reduced between two consecutive experiments. The rate and α_0 dependence on P_{O_2} is similar to that shown in Figs. 6 and 7 but the rates obtained when the oxygen content in the reactor is gradually decreased are lower than those obtained upon increasing P_{O_2}. The bottom portion of Fig. 8 contains the surface oxygen activity behavior during these experiments. The difference in rate and α_0 appears mainly in the regime of high reaction rates, i.e., between P_{O_2} = 0.005 and P_{O_2} = 0.015 bar.

DISCUSSION

The work of Kurtanjek *et al.* (*18*) indicated that the unsteady state phenomena observed during H_2 oxidation on Ni are related to oxidation and reduction of the catalyst surface. Formation of nickel oxide under reaction conditions has been well established (*4, 21, 29, 30*). Moreover Quinn and Roberts (*29, 30*) suggested that there are two types of oxide formed, stoichiometric NiO and "dilute" Ni_mO with $m \simeq 3$. Riekert pointed out that an explanation of multiplicity of steady states and sustained oscillations in catalytic reactions could be obtained if the possibility of phase transitions in the catalyst were taken into account (*31*). Based on the hypothesis of reduction–oxidation of the nickel surface, Kurtanjek proposed a mathematical model which consisted of two differential equations and described the dynamic behavior of adsorbed oxygen and surface oxide while average values for the other gas phase and adsorbed species were considered (*22*).

The experimental results presented in the previous section are shown schematically in Fig. 9a and b. Figure 9a describes the rate and α_0 behavior for constant outlet P_{H_2}. At very low P_{O_2} only stable steady

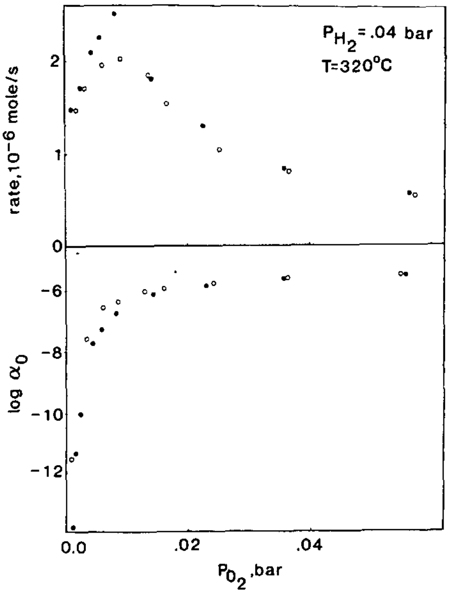

FIG. 8. Hysterisis observed on rate and α_0: filled circles, increasing P_{O_2}; open circles, decreasing P_{O_2}.

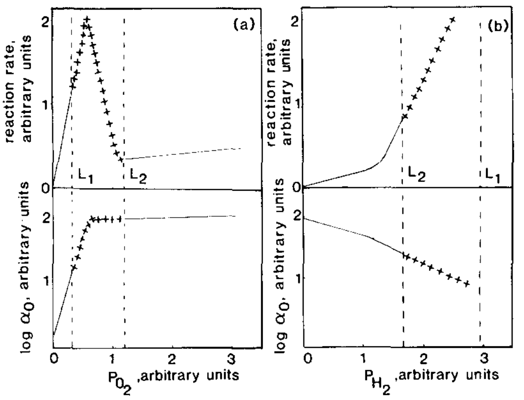

FIG. 9. Qualitative behavior of rate and α_0: effect of (a) P_{O_2} and (b) P_{H_2} on reaction rate and α_0 (arbitrary units).

states are obtained and the rate increases sharply with increasing P_{O_2} while α_0 increases drastically as well. At a given P_{O_2} (vertical line L_1) unsteady states appear. Line L_1 is close to the maximum rate attained at these T and P_{H_2} conditions. Oscillatory phenomena will appear until P_{O_2} exceeds a second limit, L_2, above which stable steady states are observed again. Both limits L_1 and L_2 move to the left with decreasing temperature. The isothermal oscillations are usually aperiodic but when transport phenomena become significant the oscillations become periodic with very short periods and the catalyst temperature fluctuates by 5–50°C. In the oscillatory regime an increase in the reaction rate corresponds to a decrease in α_0. Figure 9b shows the rate and α_0 behavior schematically for constant outlet P_{O_2}. At low P_{H_2} the rate increases with P_{H_2} with an apparent order higher than one. Stable steady states are obtained until the pressure of hydrogen exceeds a certain value which corresponds to line L_2 of Fig. 9a. Above that limit isothermal aperiodic oscillations are observed. Stable steady states will appear again when P_{H_2} exceeds a second critical value (line L_1). It was extremely difficult to obtain this second limit when the outlet P_{O_2} was kept constant (Figs. 4 and 5). This is because by increasing P_{H_2} the reaction rate increases to such high values that it is not possible to avoid the effect of external heat and mass transfer even if the total flowrate is kept at its highest possible value. The problem could be fixed if the amount of catalyst were significantly reduced. Unfortunately that was not possible either. A very small amount of catalyst would not give a nickel film of minimum thickness required to measure the open-circuit EMF of the cell. In fact the catalyst loading used was the lowest possible to ensure appropriate contact between zirconia electrolyte and nickel film electrode as well as between nickel film and nickel wire necessary to complete the electrical circuit of the cell (*21*, *28*).

Figure 9a and b combined will produce the scheme of Fig. 10a where the limits within which oscillations occur are plotted as a function of the catalyst temperature and the ratio P_{H_2}/P_{O_2} in the gas phase. A very large number of experimental data obtained over a period of more than 2 years was used to construct this graph (*25*, *26*).

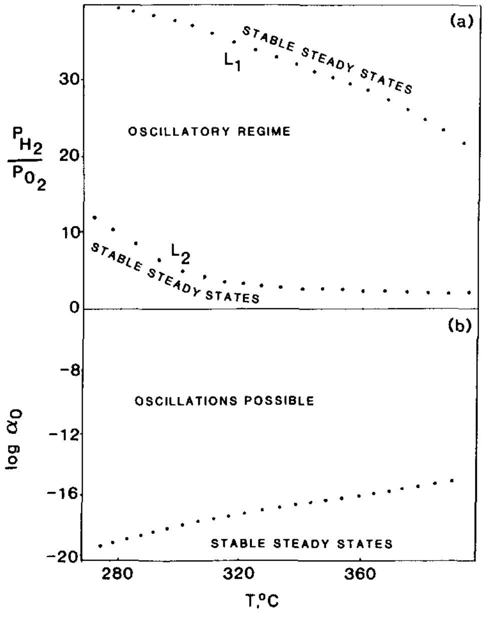

FIG. 10. Effect of gas composition and temperature on the boundaries within which oscillations occur.

Once again note that the ratio P_{H_2}/P_{O_2} refers to outlet partial pressures and should thus be independent of the reactor conversion. Figure 10b contains the minimum values of α_0 below which oscillations were not observed. Hence the curve in Fig. 10b corresponds to line L_1. There was no clear maximum α_0 value above which oscillations disappear. Therefore there is no equivalent of line L_2 on the α_0–T graph.

Figure 10 shows clearly that oscillatory phenomena will appear at a given temperature as long as the P_{H_2}/P_{O_2} ratio—and not P_{O_2} alone—lies between certain values. Kurtanjek *et al.* observed oscillations for oxygen content below 1% (*18, 19*) while Schmitz *et al.* observed oscillations for inlet oxygen as high as 5% (*17*). We observed such phenomena with outlet oxygen content as high as 8% at 400°. In that case, however, the hydrogen content had to exceeed 14% (*25*).

Figure 10 has been prepared from experimental data in which either nitrogen or helium were used as diluents. According to our measurements substitution of He with N_2 or vice versa does not affect the reaction rate or the surface oxygen activity. Kurtanjek *et al.*, however, observed changes in the CPD and in the shape of oscillations when the nitrogen content exceeded 40% in the reactor (*18*). A number of investigators have reported that nitrogen chemisorbs on nickel surfaces (*33, 34*). A low temperature chemisorption results in coverages on the order of 30% at −195°C but the coverage decreases with temperature to become essentially zero at 140°C. Nevertheless a different type of nitrogen chemisorption occurs at higher temperatures and results in nitrogen coverages of the nickel surface as high as 5% at 300°C (*33*). Again the coverage of chemisorbed nitrogen decreases with temperature. Kurtanjek *et al.* (*18*) carried out most of their experiments at 160–300°C while most of our data were obtained at 280–400°C. Especially the N_2–He substitution experiments were done at 360–400°C. Hence it may be possible that the effect of nitrogen becomes pronounced at temperatures where its chemisorption becomes considerable, i.e., below 300°C. This can explain the apparent contradiction between the present work and the work of Kurtanjek *et al.* concerning the diluent effects.

Sheintuch (*10*) pointed out that at least two rate-determining steps are required to account for oscillations in an isothermal system. The α_0 measurements substantiate this requirement as can be seen in Figs. 6 and 7. Oscillations appear at P_{O_2} very close to the value corresponding to the maximum reaction rate. In this regime the surface oxygen activity is 3 to 9 orders of magnitude lower than $P_{O_2}^{1/2}$. According to the definition of the thermodynamic activity of atomically adsorbed oxygen, $\alpha_0 = P_{O_2}^{1/2}$ if the adsorbed and gaseous oxygen are in equilibrium (*21, 28*). Therefore in the oscillatory regime the rates of adsorption of oxygen and of reaction of adsorbed oxygen with hydrogen attain comparable values.

The present results in conjunction with the work reported previously (*21*) seem to substantiate the earlier works of Kurtanjek *et al.* (*18, 19*), who proposed an oxidation–reduction scheme as the possible cause of the oscillatory behavior. Indeed, the reaction kinetics exhibit peculiar trends even in the stable steady state regime (Fig. 2). In a previous communication (*35*) a kinetic model was proposed for the present reaction system. According to that model hydrogen and oxygen adsorb dissociatively on nickel. The catalyst surface can also undergo oxidation to nickel oxide (*35*). Nevertheless, this reaction will take place only if the surface oxygen activity exceeds a minimum value α_0^*. Consequently, whenever the catalyst surface is oxidized and α_0 decreases so that $\alpha_0 < \alpha_0^*$, the oxide becomes unstable and must dissociate. Although prepared before the completion of this work the above model predicts with very good agreement the present stable steady state and oscillatory kinetic and SEP results.

The details of the dynamic model have already been presented elsewhere (*35*) and hence are not shown here. It is worth mentioning the physical interpretation of appearance and disappearance of the unsteady states.

For very low P_{O_2} the surface oxygen activity attains values below the minimum α_0^* required to form nickel oxide. Hence stable steady states are obtained and only atomic oxygen and atomic hydrogen are adsorbed on the surface. This situation corresponds to the regime on the left-hand side of line L_1 in Fig. 9a and case 1 in Fig. 11. For higher P_{O_2}, α_0 increases so that $\alpha_0 > \alpha_0^*$. Therefore formation of nickel oxide is now possible. During that process and while α_0 tends to reach a steady state value it hits the stability limit α_0^* and the oxide of the surface is quickly reduced to create "clean" nickel sites. Consequently the coverage of atomic oxygen increases drastically and therefore α_0 increases as well so that it exceeds α_0^*. Again formation of oxide starts, the system tends to reach steady state, it hits the stability limit, and the same procedure is repeated. This situation is shown schematically in Fig. 11, case 2.

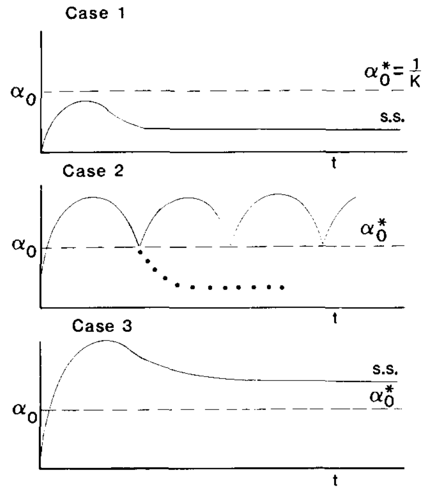

FIG. 11. Transient behavior of surface oxygen activity: case 1, very low P_{O_2} (below L_1); case 2, between L_1 and L_2; case 3, high P_{O_2} (above L_2); s.s.: stable steady state value of α_0.

When, however, the inlet P_{O_2} becomes too high the steady state value of α_0 toward which the system tends to go exceeds the stability limit α_0^* and therefore the nickel oxide that has been formed will never become unstable. Limit cycles will not appear and the surface is primarily oxidized. This case represents the stable steady states on the right-hand side of line L_2 in Fig. 9a and case 3 in Fig. 11.

Following the hypothesis of oxidation and reduction of the nickel surface, line L_1 (Figs. 9 and 10) can be interpreted as the stability limit of nickel oxide. It has been justified experimentally by means of SEP measurements (*21*) that nickel oxide forms via atomically adsorbed oxygen rather than via gaseous oxygen, i.e.,

$$m - o + m \rightleftharpoons m - o^* + m$$

where m stands for catalyst surface site and $m - o$ and $m - o^*$ correspond to adsorbed oxygen and nickel oxide species, respectively. The equilibrium constant K of the above reaction determines a temperature-dependent critical surface oxygen activity α_0^* below which the nickel oxide becomes unstable, i.e.,

$$\alpha_0^* = 1/K.$$

Figure 12 contains the experimentally observed dependence on temperature of the minimum α_0 for oscillations to appear (line L_1). Also shown on the same figure are literature values (*31, 32*) for the critical α_0^* for dissociation of nickel oxide. The two lines fall very close to each other in a wide range of temperatures. Vayenas and coworkers, who studied the oscillatory behavior of the platinum-catalyzed ethylene oxidation, proposed a similar surface oxidation–reduction model to explain their observations (*36*). Furthermore, the above authors used SEP data to determine, in very good agreement with previous workers, the stability limit of surface platinum oxide (*37*).

Hence, although not proved conclusively, the proposed interpretation of the

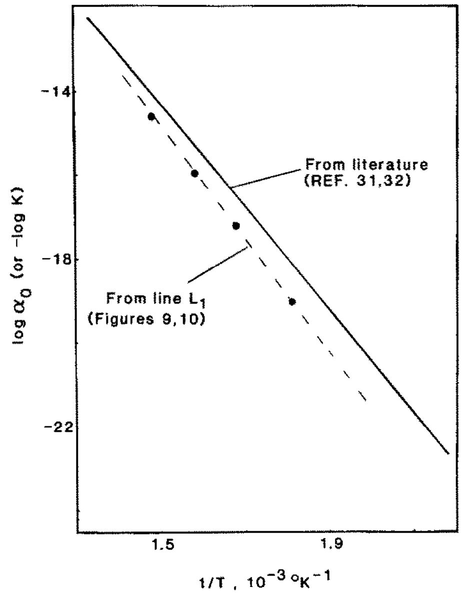

FIG. 12. Comparison of the minimum surface oxygen activity for oscillations to appear (dashed line) with the mininum surface oxygen activity for nickel oxide formation (solid line).

boundary line L_1 as the stability limit of nickel oxide receives strong experimental support with the present study.

CONCLUSIONS

In summary, the present work shows that the dynamic phenomena observed during the oxidation of H_2 on Ni are affected by the gas-phase composition of both reactants, the catalyst temperature, and also by the pretreatment of the nickel surface. The last requires a well-specified preparation of the catalyst before every experiment. Otherwise ambiguous and irreproducible results will be obtained.

In most cases the kinetic and EMF oscillations are aperiodic and turn to simple and periodic only when the effects of external heat and mass transfer become significant. In the latter case the temperature oscillations probably serve as a means of communication and synchronization of the nickel crystallites. In the case of isothermal aperiodic fluctuations one possible means of synchronization could be the uniform gaseous composition above the catalyst. This in turn suggests that the transient material balance of at least one gaseous component should be taken into account when a mathematical model is prepared.

In agreement with previous works the present results indicate strongly that the oscillatory phenomena are related to formation and reduction of a surface nickel oxide. A mathematical model prepared earlier satisfies most of the experimental observations (*35*). In view of the present experimental information the above model could be improved by introduction of a number of physically justified assumptions. Such assumptions could be the adsorption and desorption of gaseous reactants on the nickel oxide surface (not included in the original model), coverage-dependent activation energies, and multilayer oxide formation.

Oscillations during hydrogen oxidation have been observed on palladium and platinum catalysts (*38–41*). The dissociation pressures of PdO and PtO are significantly different (*31, 32, 42*) from that of NiO. Hence it seems useful to use the SEP technique to study the H_2 oxidation on Pd and Pt catalysts and compare the results with the nickel–hydrogen–oxygen system.

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