JOURNAL OF CATALYSIS **66**, 11–27 (1980)

Surface State and Kinetic Oscillations in the Oxidation of Hydrogen on Nickel

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Received October 12, 1979; revised May 8, 1980

Contact potential difference (CPD) and effluent O_2 concentration measurements were used to monitor oscillations in the surface state and reaction rate during the oxidation of hydrogen over a nickel plate in a continuous-flow reactor. Oscillatory states were observed over a wide range of temperatures (160–400°C) for mixtures containing a large excess of hydrogen. CPD measurements indicate that the system oscillates between a state in which oxygen is chemisorbed on a reduced surface and an oxidized surface state. Periodic oscillations were observed when either significant mass or heat transfer limitations existed. Aperiodic (chaotic) behavior existed when the transport resistances were small. The characteristics of the oscillatory states became independent of linear velocity and residence time in the reactor, when the transport limitations were small, indicating that the coupling between the transport and chemical rate processes is not the cause of the oscillations.

INTRODUCTION

Oscillatory behavior in heterogeneous catalytic systems attracted considerable attention in recent years and has inspired comprehensive reviews of the subject (*1*–*3*). The occurrence of isothermal oscillations seems to indicate that this behavior is caused by intrinsic kinetic rate processes rather than by the coupling between thermal transport and chemical rate processes. The knowledge of the mechanisms underlying this behavior will hopefully enable prediction of the reactions and the conditions under which oscillations occur as well as the assessment of the potential practical applications of the phenomenon.

Isothermal oscillations have been observed so far only in the oxidation of carbon monoxide on Pt, and of hydrogen on Pt, Pd, and Ni. Several kinetic mechanisms have been proposed to account for the oscillatory behavior. These were based on one of the following assumptions: (a) dependence of activation energy or heat of adsorption on surface coverage (*1*, *2*, *4*, *5*), (b) cyclic oxidation and reduction of the surface (*3*, *4*, *6*), (c) shift between multiple steady states due to a slow adsorption and desorption of an inert compound (*7*), and (d) surface temperature oscillations (*8*). A critical discrimination among the various models requires information about the dynamic state of the surface and the adsorbed species. Unfortunately, no direct information is available on the state of the surface in the course of the oscillation since in most previous studies the oscillations have been monitored by measurements of the reaction rate, gas-phase composition, or surface temperature. Belyaev *et al.* (*9*) measured simultaneous oscillations in the reaction rate and in the work function of catalytic platinum and nickel surfaces during the oxidation of hydrogen. However, they did not attempt to relate the changes in the work function to the state of the surface.

This work reports an investigation of oscillatory states observed during the oxidation of hydrogen on a nickel plate in which the state of the surface was moni-

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tored by measuring the contact potential difference (CPD) using the vibrating capacitor technique.

The knowledge of the relationship between the dynamic changes in the state of the surface and in the gas-phase composition is expected to enhance our understanding of the surface processes involved in the oscillatory behavior.

The work function of a uniform surface is defined as the difference between the potential of an electron in the bulk of the metal and one outside the surface. The CPD is defined as the difference in work function between two metals (*10*). Adsorbates modify the dipole structure of metal surfaces and change the work function. If the dipole moments of the individual complexes are independent of surface coverage, the corresponding change in the work function is equal to $\sigma\theta\mu/\epsilon_0$ (*10*), where σ is the maximal number of dipoles per square meter, θ the fractional surface coverage, μ the dipole moment in $C \cdot m$, and ϵ_0 the dielectric constant of vacuum. The work function increases when the exterior of the dipole layer is negatively charged. Thus, the presence of an adsorbate on the surface of a metal catalyst can be determined by measuring the contact potential difference between the catalyst and a metal surface inert to the reacting mixture. We adopt here the definition that a decrease in CPD corresponds to an increase in the work function of the catalyst.

A quantitative analysis of the state of the surface cannot be attained from CPD measurements due to difficulties in interpreting the signal resulting from the various surface species (chemisorbed oxygen, hydrogen, water, hydroxyl groups, and various nickel oxides). In this case, however, a qualitative analysis of the oxidation–reduction process may be carried out, capitalizing on the difference in the sign between the surface potential of chemisorbed oxygen and hydrogen (which is positive) and the surface potential of the nickel oxides (negative).

The adsorption of hydrogen and oxygen on nickel surfaces and the interactions among the three have been the subject of numerous studies, but a comprehensive review of these studies is beyond the scope of this paper. When hydrogen or oxygen is adsorbed on a nickel surface, the metal acts as an electron donor and a double charge layer is produced, with the negative charge outwards. The change in CPD upon hydrogen chemisorption on a Ni film has been found to be −0.35 V (*11*), varying from −0.195 V on Ni(111) to −0.53 V on Ni(110) crystals. Hydrogen desorbs from nickel at temperatures below 100°C (*12*).

Measurements of CPD change due to oxygen chemisorption on nickel, summarized in (*11*), fall in the range of −0.55 to −1.6 V. When a nickel film with preadsorbed oxygen is heated, the CPD usually increases due to oxidation. For example, the CPD increased after oxidation by 0.7 V at 400°K (*13*). This process is referred to as thermal regeneration (*13*).

Quinn and Roberts (*14*) claimed that the oxide found at room temperature is not a stoichiometric NiO but a "dilute" oxide, with a total oxygen uptake equivalent to two monolayers, and a corresponding CPD increase of 0.27 V. Field emission microscope studies (*15*) and observations of CPD variation during thermal regeneration at 400°K (*16*) indicate that the oxide is formed in an autocatalytic manner, and lead to the suggestion that this reaction involves nucleation and growth processes.

Several investigators have concluded that two types of oxide are formed (*14, 17*): "dilute" oxide Ni_mO ($m \sim 3$) and a stoichiometric NiO. At room temperature the reactivity of NiO with hydrogen is much smaller than that of Ni_mO. When Ni oxide is exposed to hydrogen a fast increase in CPD occurs, followed by a slow decrease. The large increase in CPD (1.0 to 1.5 V above that of Ni) is believed to result from the formation of hydroxyl groups which then react with hydrogen to form water. Benton and Emmet (*18*) found that the reduction of NiO is an autocatalytic reac-

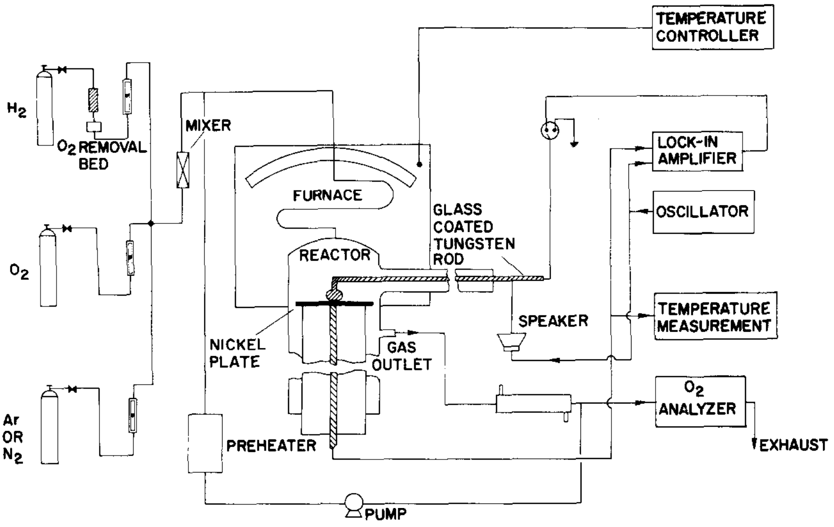

FIG. 1. Schematic of the experimental system.

tion, and implied that the Ni formed acts as an autocatalyst.

EXPERIMENTAL SYSTEM AND PROCEDURE

The experiments were carried out in the apparatus shown schematically in Fig. 1. The reaction mixture of hydrogen and oxygen was passed over a nickel catalyst whose CPD was measured by the vibrating capacitor method. The outlet oxygen concentration was measured by a Beckman Model 755 paramagnetic oxygen analyzer.

The gases, extradry-grade oxygen (minimum purity 99.6%, main impurity argon), prepurified-grade hydrogen (minimum purity 99.99%, main impurity nitrogen), and high-purity nitrogen (minimum purity 99.99%, main impurity oxygen), were purchased in cylinders from Union Carbide. The hydrogen was purified by passing through an oxygen remover (Matheson Series 64-1000) and a molecular sieve desiccant cartridge (Matheson Model 26327-10). The metered gases were mixed by passing through a 28-cm-long and 5-cm-diameter bed filled with glass beads (2-mm diameter) and preheated in an electrically heated furnace.

The reactor (Fig. 2) was made of glass and kept in a furnace heated by a 1-kW heating coil and its temperature was controlled within ±0.05°C by a proportional temperature controller (RFL Model 71A). The catalyst was a thin disk (2-cm diameter, 0.75-mm thickness) of nickel (99.98% purity) glued by cement on top of a flat glass plate. Two iron–constantan thermocouples coated with porcelain measured the temperature of the catalyst and the gas

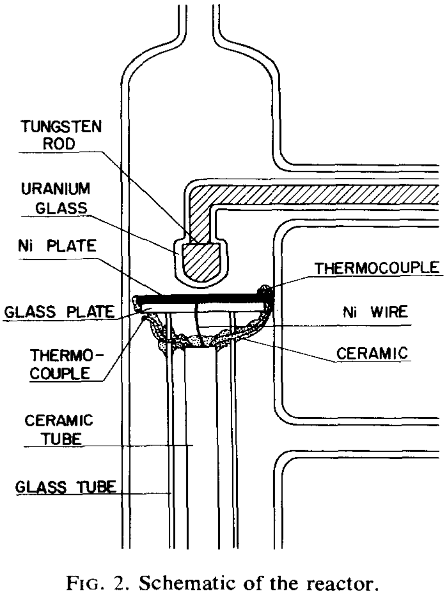

FIG. 2. Schematic of the reactor.

adjacent to it. A uranium glass-coated tungsten rod placed over the nickel plate formed the inert part of the capacitor. It was vibrated mechanically at a frequency of 270 s^{-1} by a dual-cone speaker [Component Specialists, 10 W). The rod was held at the center of a Plexiglas ring attached to a three-dimensional positioner. The average distance between the tungsten and nickel plate was about 0.5 mm and the amplitude of the oscillating tungsten rod was about 0.3 mm. Electrical oscillations generated by an electrical oscillator (Hewlett–Packard Model 201CR) were fed simultaneously to a power and a lock-in amplifier (Princeton Applied Research Model 124). Phase differences between the signal from the nickel plate and the oscillator were manually adjusted on the lock-in amplifier by searching for the maximal output. The voltage output from the lock-in amplifier, which is the contact potential difference, was fed to the vibrating side of the capacitor.

The reactor was operated either in a once-through mode or as a recirculating reactor with recycle ratios of 20.6 to 310. A bellows pump (Metal Bellows Corp. MB-158) was used to recirculate the gas. Tracer experiments indicate that the residence time density function of the reactor, when operating in a once-through mode, is very close to that of a continuously stirred tank reactor with a volume of 35 cm^3. The volume of the reactor with the recycle loop is 223 cm^3.

A chart recorder was used to record simultaneously the CPD, outlet oxygen concentration, catalyst surface temperature, and temperature difference between the catalyst and the gas phase.

New catalyst disks were cleaned and activated by heating up in hydrogen to 450°C followed by several cycles of reduction in a stream of hydrogen for 24 h and oxidation for 12 h in an oxygen stream. The surface was judged to be clean after reproducible CPD responses were obtained in successive reduction–oxidation cycles. The reduced surface was then cooled to the desired temperature in a stream of hydrogen, and oxygen was added to the feed.

At the end of each experiment the catalyst was reduced at 450°C in a stream of hydrogen for at least 12 h. This procedure yielded reproducible oscillatory behavior.

A comparison of SEM pictures of the new plate with those taken after 2 months of experimentation revealed a considerable roughening of the surface. A detailed description of the experimental system and procedure can be found in (*19*).

EXPERIMENTAL RESULTS

Oscillatory changes in CPD and outlet oxygen concentration were observed over a wide range of temperatures (160–400°C) for mixtures containing a large excess of hydrogen. Measurements of CPD and oxygen conversion of both oscillatory and stationary states were carried out over a wide range of oxygen concentrations in order to attain a better understanding of the major rate processes. In addition, CPD measurements were carried out during the oxidation and reduction of the nickel catalyst to aid in the interpretation of the CPD signal. The influence of linear velocity on the behavior of the system was investigated by varying the flow rate in the reactor, and by operating it in the recirculation mode.

Domain of Oscillatory Behavior

The behavior of the system was followed by a systematic increase of the oxygen concentration at various temperatures and flow rates. Typical results obtained at 270°C and a linear velocity of 6.38 cm/s (feed flow rate of 800 cm^3/min) in the once-through reactor are shown in Fig. 3. Starting with a surface reduced in H_2, the CPD decreased with increasing oxygen concentration. A smooth transition from a stable to an oscillatory state occurred at about 0.1 vol% O_2. The oxygen concentration corresponding to this transition is denoted by B_1. The oscillatory states observed in this case were aperiodic (also termed chaotic) characterized by peaks of varying amplitude, of

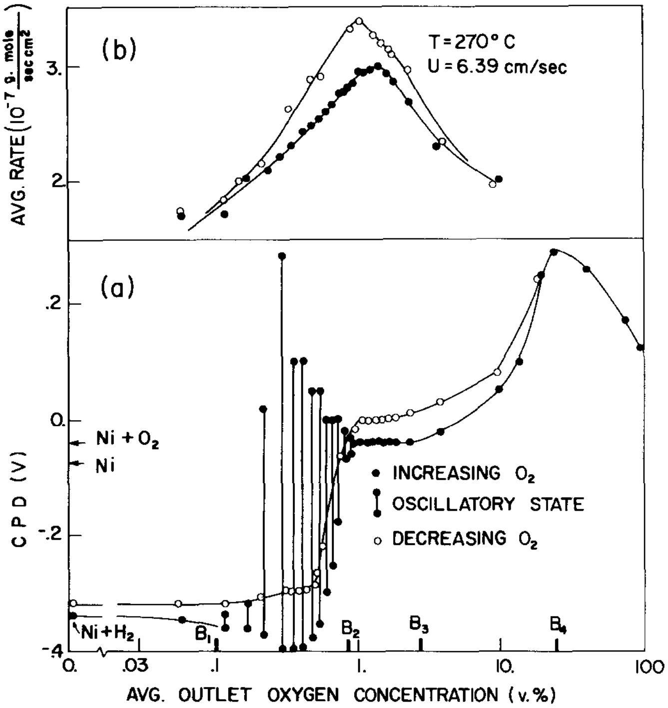

FIG. 3. Variation in CPD and reaction rate when outlet oxygen concentration is increased (solid circles) and then decreased (open circles).

the type shown in Figs. 12a and 13a. The oscillatory states are denoted in Fig. 3 by vertical lines whose endpoints correspond to the largest peak to peak amplitude. Upon an increase in the O_2 concentration the amplitude of the CPD oscillations increased, attained a maximal value at about 0.3 vol% O_2, and then decreased. A smooth transition to a time invariant state occurred at a critical O_2 concentration denoted by B_2 (about 0.90 vol% O_2). The CPD attained a rather constant level of about 0.04 V between B_2 and another transition point, denoted by B_3, at about 2.6 vol% O_2. Beyond B_3 the CPD increased monotonically and attained a maximal value at B_4 (at about 25 vol% O_2). It then decreased, attaining a value of 0.12 V at 100% O_2. Also indicated in Fig. 3a are the CPD of the reduced Ni surface following exposure to argon, which does not adsorb on Ni, and the CPD of the Ni after long exposure to pure oxygen.

A strong memory effect was exhibited by the surface. The CPD values attained upon a reduction in O_2 concentration (denoted by open circles in Fig. 3) were always higher than those attained when the oxygen concentration was slowly increased (solid circle). The CPD was measured at each point for at least 15 min, and the changes in the CPD were very slow. When the oxygen concentration was reduced to values corresponding to the oscillatory regime, oscillations appeared only after an hour and did not become fully developed until several hours later. Even then the shape and frequency of the oscillations as well as the amplitude of the CPD were different from those observed originally. A description of the slow development of these oscillations can be found elsewhere (Fig. 5 in (*20*)). The original oscillations were reproduced upon reduction of the surface and a subsequent slow increase in oxygen concentration.

Starting with a reduced surface the reaction rate increased monotonically with increasing oxygen concentration, attained a maximum at an O_2 concentration slightly

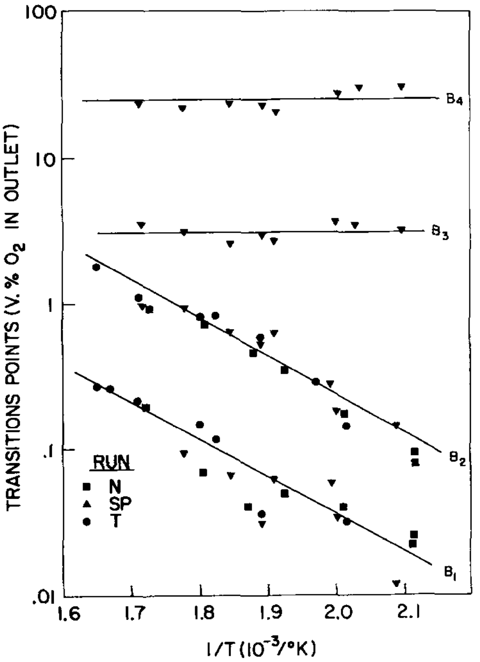

FIG. 4. Dependence of the transition points on temperature for a feed flow rate of 800 cm^3/min.

higher than B_2, and then decreased (Fig. 3b). Thus, the average reaction rate increased monotonically with increasing O_2 concentration over the oscillatory regime (B_2, B_3). Due to the high flow rate, the oscillations in the outlet concentration were of the order of magnitude of the noise level of the oxygen analyzer (10–20 ppm), so that they could not be investigated in this case. Surface temperature oscillations were not detected in this run, indicating that they are smaller than 0.03°C.

The characteristic behavior shown in Fig. 3 was observed over a wide range of temperatures, flow rates, and diluent concentration (of either nitrogen or argon).

The transition concentrations B_1 and B_2, which bound the oscillatory regime, were shifted to higher O_2 concentration with increasing temperatures (Fig. 4). The activation energies associated with the dependence of B_1 and B_2 on temperature were about 50 J/g · mole. Transition points B_3 and B_4 were essentially independent of temperature. The data presented in Fig. 4 were obtained with two different Ni plates over a time span of over a year. Yet, the domain of oscillatory behavior was similar in all runs.

When a stream of hydrogen and oxygen was diluted by nitrogen at 270°C and a linear velocity of 6.38 cm/s the behavior was very similar to that shown in Fig. 3a. However, for very low O_2 concentrations the introduction of the N_2 reduced the CPD, indicating that N_2 was partially adsorbed on a reduced surface. Introduction of up to 42 vol% N_2 had only a minor effect on the transition points and the maximal reaction rate. For N_2 concentrations between 42 and 85.5 vol% the transition points were shifted to higher O_2 concentration, and the maximal reaction rate decreased with increasing N_2 concentration. The frequency of the oscillations decreased in general with increasing N_2 concentration. At N_2 concentrations larger than 40 vol% the CPD oscillations became simple (single peak per cycle), of the type shown in Fig. 6, and a high CPD level was attained for a larger fraction of the period.

Characteristics of Oscillatory States

Simple oscillations existed at low flow rates for which appreciable mass transfer resistances existed. They occurred mainly at the temperature range of 160–240°C, but were observed also at higher temperatures when the heat transfer resistance led to relatively large temperature oscillations (>1°C). Multipeak oscillatory and chaotic behavior occurred mainly at high linear velocities for which the mass transfer re-

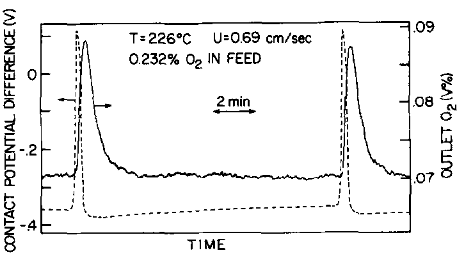

FIG. 5. Simple oscillations of CPD and outlet oxygen concentration for a low temperature and a low flow rate.

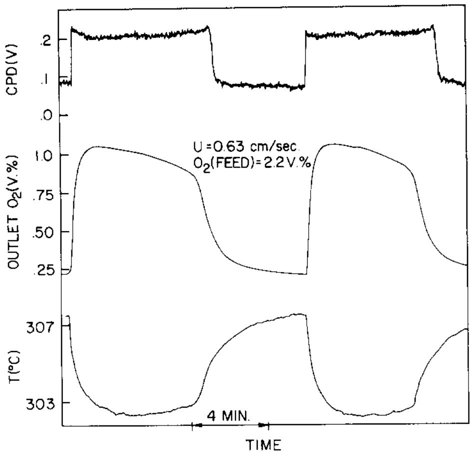

FIG. 6. Simple oscillations of CPD, outlet oxygen, and temperature for a high temperature and a low flow rate.

sistance was small and at the temperature range of 250–400°C. Temperature oscillations associated with chaotic behavior were of small amplitude (<0.3°C).

A typical simple oscillation in the CPD and outlet oxygen concentration is described in Fig. 5. During a large fraction of the cycle, the catalytic activity was high (low outlet oxygen concentration). The shift between the peaks of the two signals is due to the distance between the recording pens and the time lag for flow between the outlet of the reactor and the oxygen analyzer. No time lag was detected between these two signals when both effects were compensated for. This observation applies for most of the recorded oscillatory states. Due to the low temperature and the corresponding low reaction rate the surface temperature remained constant throughout the cycle.

Figure 6 describes simple oscillations at high temperature and low linear velocity. The high reaction rate and the large heat transfer resistance caused oscillations of 5°C in the surface temperature. The transitions of the O_2 signal between the two limiting concentration levels (52 to 88% conversion) were not as sharp as those of the CPD due to oxygen mixing in the reactor and dispersion in the tube leading to the detector. In the experiments described in Figs. 5 and 6, the average reaction rate was about 0.4 of the limiting asymptotic rate attained at sufficiently high temperatures.

At high temperatures and flow rates aperiodic or chaotic behavior of the type shown in Fig. 7 were observed. The fluctuations were rapid, with an almost constant frequency, but the amplitudes of both the CPD and the outlet O_2 concentration changed in a similar but irregular fashion. Small surface temperature oscillations with an amplitude of less than 0.2°C were noted during this experiment. Periodic oscillations were observed near the transition points B_1 and B_2 even at high temperatures and flow rates (e.g., Fig. 13a).

In certain cases no clear correspondence exists between the CPD and the oxygen oscillations (Fig. 8). While no claim can be made concerning the periodicity of the signals they resemble the superposition of a primary regular cycle with a surprisingly long period (26 min) and a secondary irregular cycle. No correspondence existed between the secondary CPD and O_2 oscillations.

Figure 9 illustrates a case in which the behavioral features of the CPD and outlet O_2 oscillations were different. While the CPD oscillation was simple, the corresponding O_2 signal had several peaks per cycle. The average reaction rate for the experiments shown in Figs. 8 and 9 was less than 0.2 of the limiting mass transfer rate.

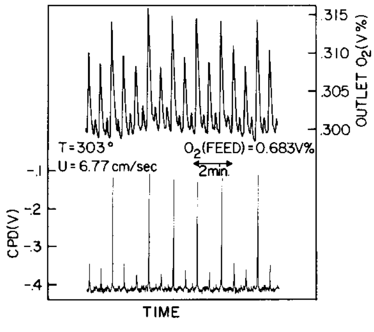

FIG. 7. Aperiodic (chaotic) variations of CPD and outlet oxygen concentration at high temperature and flow rate. Feed oxygen concentration 0.809 vol%.

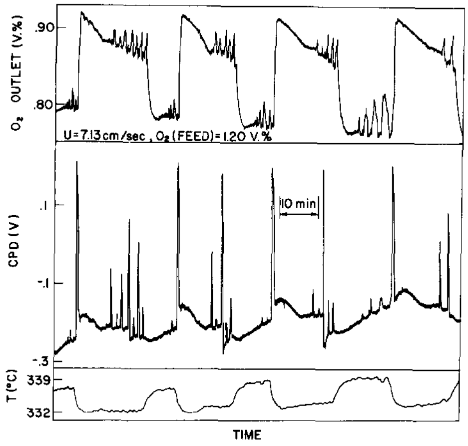

FIG. 8. Complex oscillations of outlet oxygen, CPD, and surface temperature.

When the effluent's thermal conductivity was measured by a Micro-Cell (Gow-Mac Instrument Co. Model 10-470) placed right at the exit of the reactor, the frequency of the oscillations was higher than that observed by the oxygen analyzer. The improved resolution attained by the thermal conductivity measurement was due to the shorter time constant of the thermistor and to the reduced dispersion between the outlet of the reactor and the detector.

The period of the oscillations observed in most experiments was of the order of minutes. In a special case a partially pretreated catalyst yielded very fast and almost sinusoidal CPD oscillations with a period of 1.5 s at 346°C and a linear velocity of 7.29 cm/s. A detailed description of other oscillatory states is reported in (*19*).

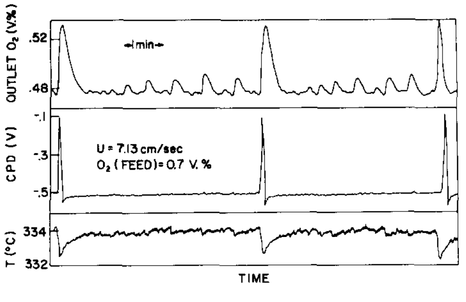

FIG. 9. Periodic oscillations of outlet oxygen, CPD, and temperature.

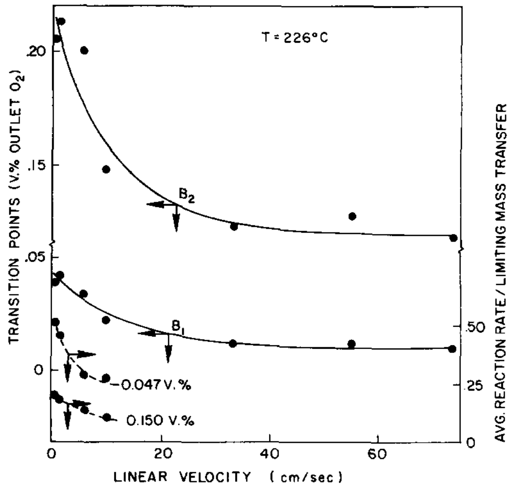

FIG. 10. Dependence of the boundaries of the oscillatory region and of the ratio of average reaction rate to limiting mass transfer rate on linear velocity.

Effect of Linear Velocity

At low gas flow rates the oscillatory regime was shifted to lower outlet oxygen concentrations with an increase in linear velocity. Above a certain critical velocity the boundaries of the oscillatory regime were insensitive to changes in the velocity. A typical example for 226°C is shown in Fig. 10. Here constant CPD periods and amplitudes were attained for velocities exceeding 33 cm/s. The CPD amplitude decreased from 490 mV at 0.69 cm/s to 180 mV at high flow rates (Fig. 11). While simple oscillations were attained for low gas velocities (Fig. 5), chaotic behavior was attained for gas velocities exceeding 10 cm/s.

The transition points shown in Fig. 10 were determined from CPD measurements because at high flow rates, the amplitude of the effluent oxygen concentration oscillations were of the same order of magnitude as the noise level of the oxygen analyzer (10–20 ppm). These results were obtained by a series of runs in which the oxygen level was changed at a fixed flow rate. In all these experiments the CPD and oxygen oscillations started smoothly at B_1, attained a maximal value at some intermediate con-

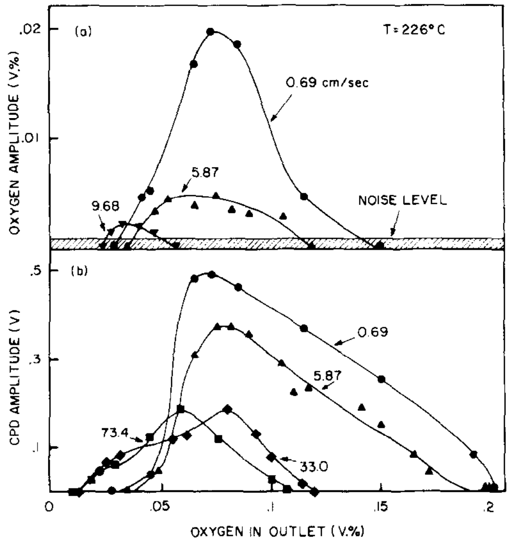

FIG. 11. Dependence of the amplitudes of outlet oxygen concentration and CPD oscillation on average outlet concentration and flow rate.

centration, and then disappeared smoothly (Fig. 11). In this case the fractional conversion amplitude, defined as the ratio of the maximal peak to peak to average conversion, increased from 0.13 to 0.15 and 0.18 as the velocity increased from 0.68 to 5.87 to 9.68 cm/s, respectively. However, the increase in the flow rate decreased the magnitude of the concentration oscillations and made them undetectable at high velocities. The O_2 concentration oscillations became undetectable or disappeared before B_2.

The maximal rate of mass transfer at any oxygen concentration could be determined from the asymptotic reaction rate attained at sufficiently high temperatures. While this limiting rate increased linearly with oxygen concentration, the average reaction rate in the oscillatory regime had a much weaker dependence on the oxygen concentration. Consequently, the influence of mass transfer limitations decreased with increasing concentrations in the oscillatory regime. For example, at 226°C and a linear velocity of 5.87 cm/s the average reaction rate was 0.3 of the limiting mass transfer rate for effluent O_2 concentration of 0.047 vol%. However, this ratio decreased to 0.14 at the oxygen concentration of 0.15 vol% (Fig. 10). At 275°C the reaction rate in the oscillatory regime was several times higher than that at 226°C; however, this behavior occurred at higher oxygen concentrations and higher limiting mass transfer rates. Thus, while the mass transfer limited the reaction rate below B_1 (0.05 vol% O_2) for a linear velocity of 6.75 cm/s, the ratio of the average reaction rate to the limiting mass transfer decreased to 0.25 at 0.2 vol% and to 0.12 at B_2 (0.6 vol%).

In order to assess the influence of complete internal mixing, experiments were conducted at 275°C with the reactor operating in the recycle mode at a fixed linear velocity of 250 cm/s. The dependence of the CPD and the average reaction rate on the effluent oxygen concentration, as well as the region of O_2 concentration for which oscillations existed, were the same as those of a reactor operating in the once-through mode at a linear velocity of 6.45 cm/s.

When the reactor was operated in the recycle mode the frequency of the CPD oscillations was several times higher than that in the once-through mode at the same outlet O_2 concentration (Figs. 12, 13). The CPD oscillations in the recycle mode were

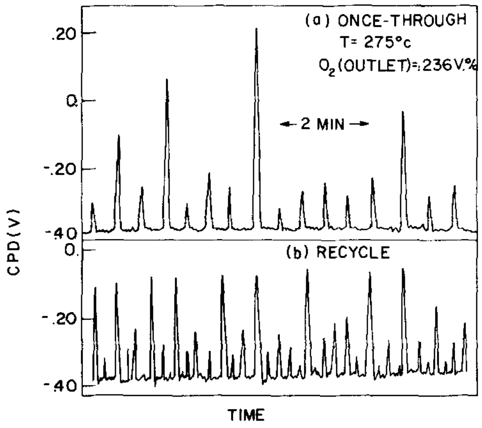

FIG. 12. Aperiodic CPD attained in the (a) once-through mode of operation (U = 6.45 cm/s) and (b) recirculating mode (U = 250 cm/s) under the same operating conditions (flow rate 800 cm^3/min; feed oxygen 0.367 vol%, outlet oxygen 0.236 vol%).

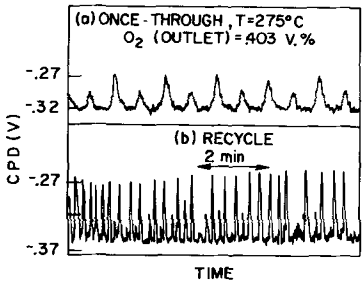

FIG. 13. CPD of (a) periodic state attained in the once-through mode of operation (U = 6.75 cm/s) and (b) aperiodic state obtained in the recirculating mode (U = 250 cm/s) under the same operating conditions (feed flow rate 800 cm^3/min; feed oxygen 0.63 vol%, outlet oxygen 0.47 vol%).

aperiodic even when periodic oscillations existed for the once-through operation at the same oxygen concentration (close to B_2). No corresponding oscillations in either the oxygen concentration or the surface temperature could be detected for both modes of operation at 275°C.

A special set of experiments was carried out with the reactor operating in the recycle mode at a constant linear velocity of 250 cm/s and feed rates between 100 and 1500 cm^3/min (corresponding to gas residence times of 72.7 to 4.8 s). The CPD amplitude and frequency and the oscillatory region depended only on the outlet oxygen concentration and were independent of the gas residence time in the reactor.

Correspondence between CPD and Oxygen Oscillations

At velocities below 1 cm/s simple oscillations were attained and for each CPD peak a corresponding peak in the oxygen concentration existed (Figs. 5 and 6). At high velocities and temperatures in the range of 226–275°C oxygen oscillations could not be detected over part or the whole region in which CPD oscillations were observed (Fig. 11). At 335°C CPD and oxygen oscillations were noted over the same concentration region, but the correspondence between the two signals was either poor (Fig. 8) or nonexistent (Fig. 9).

In a series of runs carried out at 280–305°C and a linear velocity of 6.77 cm/s oxygen oscillations were observed for oxygen concentrations exceeding B_2, i.e., in the region in which the CPD was time invariant (Figs. 14a and b). In these surprising cases, the graphs of the amplitude of the oxygen oscillations attained a local minimum close to B_2. The corresponding temperature oscillations were small (less than 0.2°C).

The CPD oscillations were of the type shown in Fig. 7 for most of the oscillatory region, with a close correspondence between the O_2 and the CPD signals. As the oxygen concentration approached B_2 the amplitude of the CPD oscillations became more uniform (Fig. 15a), and close to B_2 the CPD oscillations became periodic with a constant amplitude (Fig. 15b). Close to B_2 the oxygen oscillations resembled the superposition of two periodic signals, one having the same period as the corresponding CPD oscillations (period of about 30 s) and one with a larger amplitude and a period of about 4 min. Figure 15c illustrates the oxygen oscillations which were attained for O_2 concentrations exceeding B_2. The ratio of the average reaction rate to the limiting mass transfer rate was about 0.25, 0.22, and 0.16 for cases a, b, and c of Fig. 15.

At low linear velocities and high temper-

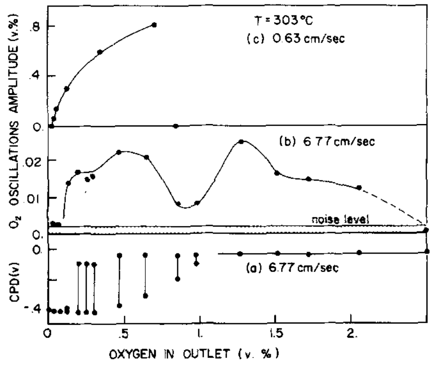

FIG. 14. Dependence of CPD and oxygen oscillations on outlet oxygen concentrations and linear velocity at 303°C.

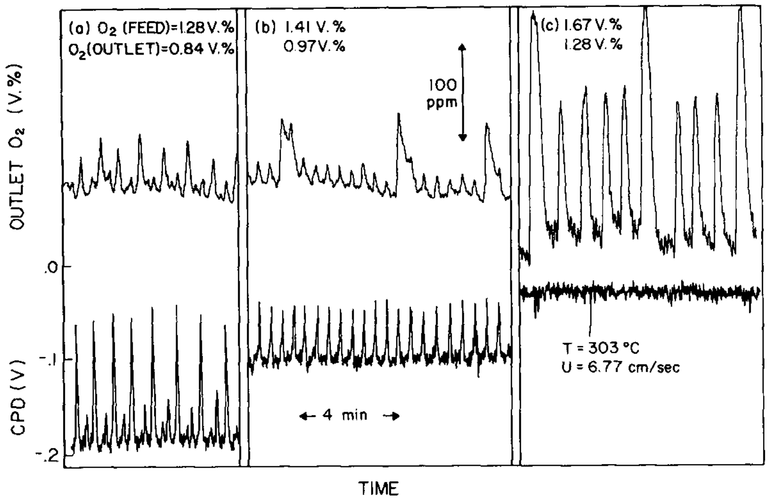

FIG. 15. Oscillatory states observed near the transition point B_2 at 303°C and a linear velocity of 6.77 cm/s.

atures, temperature oscillations of the type shown in Fig. 6 accompanied the CPD and oxygen oscillations. For example, temperature oscillations of up to 5°C were noted at 303°C and a linear velocity of 0.63 cm/s. The amplitude of the oxygen oscillations in this case was rather large (Fig. 14c) and increased monotonically with increasing oxygen concentration (maximal amplitude was 8250 ppm). Beyond a critical oxygen concentration both CPD and oxygen oscillations disappeared simultaneously. The maximal fractional amplitude conversion in this case (0.55) is significantly larger than that observed at the same temperature and a linear velocity of 6.77 cm/s (less than 0.065).

Similar behavior to that shown in Fig. 15c was noted at 335°C and a linear velocity of 6.77 cm/s. The oscillations were regular and accompanied by large temperature oscillations (Figs. 8 and 9).

Identification of Surface States

Mixtures of either oxygen or hydrogen in argon (whose adsorption on Ni at 270°C is

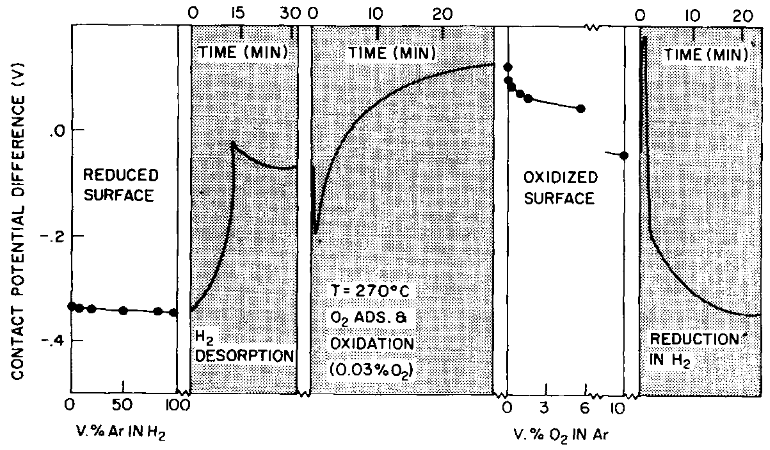

FIG. 16. Identification of stationary and dynamic surface states.

negligible) were fed to the reactor, and the CPD was measured as a function of the composition (Fig. 16) in order to determine the contribution of the adsorbed species to the CPD. Starting with a reduced surface, the CPD was independent of the composition of the H_2–Ar mixture. However, for a pure argon mixture the CPD increased to −0.074 V. When a mixture of 0.03 vol% O_2 in argon was passed over the Ni plate, the CPD decreased slowly, reaching −0.21 V within a minute. The CPD then increased asymptotically to 0.125 V, which is 0.2 V more positive than the CPD of Ni in argon. The CPD decreased with increasing O_2 concentration and became −0.04 V at 100% O_2. Subsequent exposure of the oxidized surface to hydrogen caused a rapid increase of the CPD to +0.18 V followed by a slow decrease to the original value of the reduced metal.

Similar behavior occurred when oxygen was introduced into the hydrogen stream after the metal was reduced. The CPD increased rapidly by 0.45 V over a period of a few seconds followed by a slow decrease and onset of oscillations after about 3 min.

DISCUSSION OF RESULTS

Identification of Surface States

A major aim of this study was to attain a better understanding of rate processes occurring on the catalytic surface during the oscillations. The experiments described by Fig. 16 were carried out to identify the various surface states.

The constant CPD attained for mixtures of hydrogen in argon indicated that a constant surface coverage (most probably a monolayer) of hydrogen existed over the whole range of H_2 concentrations. The hydrogen adsorption decreased the CPD of clean nickel, which was 0.074 V, by −0.27 V.

The variation in CPD following exposure of the surface to oxygen may be interpreted as follows: oxygen was initially adsorbed on the surface leading to an increase in the work function (decrease in CPD). This was followed by formation of a surface oxide and an increase in CPD. The experiments indicate that both adsorption of oxygen and surface oxidation were rather slow processes at 270°C and are likely to be rate determining. Transient CPD measurements at lower oxygen pressures revealed an inflection point shortly after the start of the adsorption, suggesting that the process was autocatalytic.

The decrease of the CPD with increasing oxygen concentration in argon suggests that oxygen is adsorbed on the oxide. This conjecture is supported by the fact that when the oxygen stream was replaced by argon, the CPD increased rapidly by 0.075–0.1 V, indicating a fast desorption of oxygen from the oxidized surface.

The transient CPD attained by us for the reduction of the oxidized surface by hydrogen is similar in shape to that attained by other investigators (*14, 17*), who attributed it to hydroxyl formation followed by reduction and chemisorption of hydrogen. The CPD attained at the end of this series of experiments was equal to the initial value, suggesting that the oxidation–reduction was completely reversible under the conditions employed.

The CPD measurements conducted by us under atmospheric pressure are in good agreement with those of other studies carried out at low pressures (*11, 13, 14*). The contribution to CPD of either oxygen adsorbed on a reduced surface or hydrogen adsorbed on oxidized Ni could not be determined from the experiments since other processes (oxidation or reduction) occurred simultaneously. The main conclusion of our experiments is that the contribution to CPD of adsorbed hydrogen or adsorbed oxygen is negative, while the CPD of nickel oxide and of either hydrogen or oxygen adsorbed on the oxide is larger than that of Ni.

Mechanism of Oscillatory Behavior

For oxygen concentrations lower than B_1 the CPD decreased with increasing O_2 partial pressure. This was probably due to an increase of fractional surface coverage by chemisorbed oxygen. This explanation is supported by observations of other investigators (*11*) that the surface potential of chemisorbed oxygen on Ni is higher than that of chemisorbed hydrogen.

In the oscillatory regime (B_1, B_2) the CPD oscillated between a negative lower level, corresponding to a state of chemisorbed oxygen and hydrogen on Ni, and an upper peak, whose CPD was usually positive, corresponding to an oxidized state. The increase in the CPD amplitude between B_1 and 0.3 vol% O_2 suggests that an increased fraction of the surface was oxidized during the oscillations. Beyond 0.3 vol% the surface was only partially reduced in the course of the oscillations.

Each oscillation consisted of several steps. The reduced surface was initially covered by chemisorbed oxygen which reacted slowly and formed a "dilute" nickel oxide by place exchange with nickel atoms. The appearance of Ni cations on the surface led to a slow increase in the CPD. At a certain critical oxide concentration the process became autoaccelerating, leading to a rapid surface oxidation and a fast decrease in the reaction rate. This accelerating oxide formation may be attributed to a nucleation and growth mechanism (*15*). In some cases the CPD of this less active state became larger than that of the oxide formed in a stream of oxygen (Fig. 16), suggesting that the oxidized surface was probably partially covered with hydroxyl ions. The decline in reaction rate associated with the oxide formation may be due to either a lower activity of the oxide or inhibition by adsorbed hydroxyl ions and/or water. The following reduction step was also fast and of an autoaccelerating nature, which may be attributed to a reaction occurring along the perimeter of oxide islands with hydrogen adsorbed on the reduced sites (*21*). The main conclusion of these measurements is that the system oscillated between a state of chemisorbed oxygen on a reduced surface and an oxidized surface state.

The cyclic behavior consisted of some very rapid and some slow steps resembling relaxation oscillations. Similar behavior was observed in many other oscillating systems (*1*, *22*).

The surface oxidation and reduction rates became faster with increasing temperatures, resulting in a higher frequency. The increase with temperature of the limiting oxygen concentration above which oscillations existed suggests that the activation energy of the reduction step was higher than that of the oxidation. This conclusion is supported by the shape of the oscillations; at low temperatures the reduction was slow relative to the oxidation step (Fig. 5), while both processes were fast at higher temperatures (Figs. 7 and 12). The positive surface potential attained in region III (B_2, B_3) is higher than that of Ni and lower than that observed during the oxidation of Ni under the same oxygen concentrations (Fig. 16), suggesting that either the presence of hydrogen affects the state of the oxidized surface or the surface is only partially oxidized. The rather constant CPD attained in this region, even though the reaction rate depended on oxygen gas concentration, is rather surprising. One possible explanation is that of a compensation among the contributions of the various species to the CPD, such as an increased nickel oxidation (positive contribution) and oxygen chemisorption (negative contribution).

The increase in CPD with increasing O_2 concentration in region IV (B_3, B_4) may be due either to formation of another oxide with a higher CPD than that formed in region III or to increasing coverage of the oxide by chemisorbed hydroxyl and/or water molecules. When the hydrogen concentration in the mixture was reduced to zero, the CPD was about 0.12 V (Fig. 3). This value is above that of the oxide formed in a stream of oxygen (Fig. 16), indicating the existence of at least two different types of oxides.

The experiments revealed that as the time in which the surface is kept in region

III is increased, a longer induction time was required for the appearance of oscillations in region II. Moreover, following a decrease in the oxygen concentration, higher time-averaged CPD and reaction rates and smaller CPD amplitudes were attained as compared to those for increasing oxygen concentrations. This "memory" of the surface may be explained by a slow transition between different oxides.

The occurrence of oxygen oscillations without accompanying CPD oscillations in part of region III (B_2, B_3), for high flow rates and temperatures in the range of 280–303°C, is most puzzling (Fig. 14). The existence of a minimum in the amplitude of the oscillations next to B_2 (Fig. 14), and the change in the shape and frequency of the oxygen oscillations next to B_2 (Fig. 15), suggests that different mechanisms are responsible for the oscillations in regions II and III.

We have no satisfactory understanding of this observation and present some conjectures concerning its occurrence. A possible explanation for the lack of CPD oscillations is that this behavior was in a region in which the CPD was insensitive to changes in the state of the surface. Another conjecture is that local oscillations in the reaction rate occurred in a region which is not covered by the Kelvin probe (it covers about 0.1 of the catalyst surface area). This nonuniform reactivity of the surface might have been induced by variations of transport resistances over the surface.

Influence of Linear Velocity

For large flow rates the transition points (B_1 and B_2), the period, and the amplitude of the oscillations were insensitive to variations in the flow rate (Fig. 10). These results indicate that coupling between transport and reaction rate processes is not required for the appearance of oscillatory states. However, heat and mass transfer resistances may affect the shape and frequency of the oscillations.

All previously reported studies claimed that the oscillations disappeared when the flow rate exceeded a critical level (*1*, *22*). Our studies indicated that this occurred for certain oxygen concentrations (above 0.11 vol% at 226°C). However, there exists a region of oxygen concentrations (for example, 0.01 to 0.11 vol% at 226°C) for which the oscillations did not disappear with an increase in the velocity. This result is supported further by the observations made at 275°C that the oscillatory regime did not vary upon an increase in the linear velocity from 6.45 cm/s in the once-through mode of operation to 250 cm/s in the recycle reactor. These findings illustrate the advantage gained by use of CPD measurements, as oscillations in the gas composition became undetectable at high linear velocities.

Most previous studies of oscillations in stirred tank reactors indicated that the period of the oscillations was of the order of the magnitude of the residence time (*1*). Our experiments with a recycle reactor, operating at a high velocity of 250 cm/s, revealed that the amplitude and the features of the oscillations were independent of a 15-fold variation in the feed flow rate.

Three competing reactions occur in the system: nickel oxidation, nickel reduction, and hydrogen oxidation on the reduced and oxidized fractions of the surface. The rates of hydrogen and nickel oxidation may be limited by the rate of oxygen transfer to the surface. The rate of reduction may be limited by the rate of water removal from the surface, if this rate process is inhibited by water as suggested by others (*18*).

In the oscillatory regime the surface state remains in a reduced state for a large fraction of the cycle (e.g., Fig. 12a). Thus, the time-averaged rate is a good approximation of the hydrogen oxidation rate. The data shown in Fig. 3 indicate that the reaction rate depends rather weakly on the gas-phase oxygen concentration in the oscillatory regime. (This dependence may be approximated by a reaction of order 0.2 in oxygen.) We were unable to determine the dependence of the nickel oxidation and reduction rates on oxygen and hydrogen concentrations. However, oscillatory states require the existence of some highly nonlinear kinetic step such as a high-order, autocatalytic surface oxidation and/or reduction step.

In the regime in which the mass transfer is not negligible an increase in the flow rate may increase the overall reaction rate and consequently the frequency of the oscillations. Changes in mass transfer limitations affect more strongly reactions with high orders. Thus, the autocatalytic surface reactions are expected to be more sensitive to variations in the linear velocity than the hydrogen oxidation reaction.

The above arguments explain the observed increase in the average reaction rate and frequency of the oscillations at 226°C with increasing flow rate (Fig. 11), as well as the higher frequencies and the changes in the shape of the CPD signal observed at 275°C in the recycle reactor in comparison with the once-through mode of operation (Fig. 12). The insensitivity of the average reaction rate to the large change in the velocity between the recycle and the once-through operations (Fig. 12) is due to the low order of the hydrogen oxidation reaction[3].

The oxygen oscillations may become undetectable either when the amplitude of the change in the gas-phase composition is within the noise level of the oxygen analyzer, or when the time the surface stays at the low-activity state is smaller than the time constant of the oxygen analyzer (about 5 s) or much smaller than the residence time in the reactor. In the recycle mode, the residence time in the reactor corresponding to feed flow rates of 100 and 1500 cm^3/min at 275°C are 72.7 and 4.8 s, respectively. The duration of the CPD spikes in the case shown in Fig. 12b is 8 s, and averaging and dilution account for the lack of observed oxygen oscillations in the recycle reactor.

The oscillations tended to be more chaotic with increasing temperatures, and the times associated with the sharp increase and decrease of CPD became shorter. However, the amplitude of oxygen concentration oscillations increased with temperature. These antagonistic effects explain the observations that while oxygen oscillations were not detected at 270 and 275°C, they were detected at higher and lower temperatures (303°C, Fig. 7, and 226°C, Fig. 11).

Communication and Synchronization

Some form of communication must exist among various points on the surface as otherwise CPD and oxygen concentration will be time-invariant averages of a large number of independent oscillators. This synchronization may be established either by heat conduction when the reaction rate oscillations are sufficiently large to cause temperature variations, by changes in the gas-phase concentration, by propagation of electric charge changes induced by changes in the state of the surface, by surface diffusion of species, or by an autocatalytic reaction mechanism which causes a rapid propagation of a local perturbation.

At high temperatures and low gas linear velocities the rate of heat generation is high, while the rate of heat removal is not sufficient to maintain the surface under isothermal conditions. The induced temperature fluctuations synchronize the reaction at various points and lead to rather regular oscillations of the type shown in Fig. 6.

The synchronizing influence of surface temperature oscillations caused the fractional conversion amplitude at 303°C and low flow rates to exceed by an order of magnitude that obtained at higher flow rates (Fig. 14). This suggests that at the low flow rate a larger fraction of the surface participates in the synchronized oxidation–reduction cycle than at the high

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[3] For the conditions of Fig. 12a, the average reaction rate at the once-through mode is about 0.15 of the limiting mass transfer rate. Elimination of this mass transfer resistance for a reaction of order 0.2 would increase the rate by only 3%, which is within the experimental error.

flow rates. The synchronizing influence of surface temperature oscillations, even just of several degrees, is probably responsible for the regular oscillations observed in previous studies of almost isothermal oscillations (*1*, *2*, *23*).

Coherent oscillations involving the entire catalytic surface are possible if the propagation velocity of a local excitation is fast enough to sweep the system at a time much shorter than the period of the oscillations. The order of magnitude of the characteristic velocity of such an excitation is $(Dk)^{0.5}$, where D and k are the diffusivity and rate constant of the autocatalytic variable, respectively (*24*). When the oxygen concentration is the autocatalytic variable in an isothermal system, fast communication may be established through the gas phase if the amplitude of the oxygen oscillation is sufficiently large. The simple oscillation observed at low temperatures and flow rates (Fig. 5) may be due to this form of communication. At high flow rate of the gas phase the concentration fluctuation becomes rather small and the communication is probably established by the propagation of an autocatalytic species on the surface. The aperiodic behavior observed at high flow rates (Figs. 7 and 12) may be due to insufficient synchronization among different locations on the surface.

A recent theoretical analysis by Sheintuch and Pismen (*24*) of communication and synchronization on isothermal catalytic surfaces indicates that inhomogeneous surface states may exist for an oscillating reaction with rates and periods comparable to those observed in this study. This inhomogeneity may explain both the disappearance of reaction rate oscillations while CPD oscillations exist, and the disappearance of local CPD oscillations while oscillations in the overall reaction rate persist.

CONCLUDING REMARKS

The contact potential difference was helpful in elucidating the various surface states and rate processes occurring during the oxidation of hydrogen on nickel. The oscillations observed at intermediate oxygen concentrations are due to a transition between chemisorbed oxygen on a mainly reduced surface to an oxidized surface state. While an interaction between transport phenomena and chemical reaction rates is not the cause of these oscillations, this interaction may affect the degree of synchronization among the various points on the surface, and thus affect the shape, amplitude, and frequency of the oscillations.

The observation that oscillations in the state of the surface exist under conditions in which oscillations in the gas phase were not detectable with the oxygen analyzer, suggests that oscillatory behavior may exist in a much larger number of catalytic systems than that known presently.

An interesting question is what, if any, may be the potential applications of the oscillatory behavior. One possible, even though difficult, application may be the nontrivial coupling of several reactions so that the energy or species generated by an oscillatory reaction will promote a reaction which cannot proceed by itself under the same conditions. This goal may be rather ambitious, but it is well known that enzymatic systems are capable of such a task.

ACKNOWLEDGMENT

We are grateful to the Welch Foundation for support of this research.

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