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Steady State and Transient Oscillations in NH_3 Oxidation on Pt[1]

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Sustained oscillations of catalyst temperature have been observed in NH_3 oxidation on Pt wires and foils in a 1-atm flow reactor. Simple and complex oscillations with periods from <1 sec to several minutes were obtained for gas compositions between 20 and 40% NH_3 in air. These depend sensitively on gas composition, flow velocity, and geometry. Oscillatory behavior is quite stable over short times, but over several hours patterns evolve slowly. Upon perturbation of composition, the average temperature is observed to attain a new steady state much more rapidly than the oscillation pattern. This is a complex reaction system in that several reactions occur, heat and mass transfer are important, and natural convection and homogeneous reaction are significant under some conditions. However, results were quite reproducible between specimens, and overall behavior exhibits clear evidence of the importance of surface processes in oscillations.

INTRODUCTION

Simple periodic and complex oscillations in catalyst temperature and reaction species concentration have been observed in several catalytic reaction systems with steady inlet flow conditions (*1*). The heterogeneous reactions studied to date are the N_2O decomposition, CO oxidation, and H_2 oxidation on several transition metals. Low-temperature H_2 and CO oxidations are probably the simplest systems because they presumably involve a small number of intermediates, and reaction conditions are almost isothermal. However, even for these reaction systems no unequivocal explanations have as yet been given for oscillations, and no models have been entirely satisfactory in explaining data. Repetition and reproducibility of observations have not been high in any of these systems, and neither the catalyst surfaces nor the reactors have been well characterized experimentally.

We report here an experimental study of the temperature response of Pt wires and foils used to catalyze ammonia oxidation. This is admittedly a rather complex system in that it involves a fast exothermic reaction with several possible chemical steps, intermediate species, and side reactions. However, the present system has been studied extensively, rates are quite reproducible, and all parameters (feed gas temperature and composition, flow rate, catalyst temperature, etc.) can be varied over wide ranges.

To our knowledge, this is the first report of periodic catalyst temperature oscillations during the oxidation of ammonia with air. However, observations of high-frequency random temperature fluctuations of the Pt–Rh gauzes used for this reaction in industrial converters are an old phenomenon referred to as flickering. In laboratory studies, Luss and co-workers (*2, 3*) have used single Pt wires in a turbulent flow field simulating industrial conditions to catalyze the oxidation of ammonia (as well as hydrogen and butane). They observed flickering of the wire temperature which they could explain as arising from fluctuations in the gas concentration close to the wire.

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EXPERIMENTAL

Mixtures of NH_3 and air at total flow velocities of 4–6 cm sec^{-1} flowed upwards in a vertically oriented Pyrex tube reactor, 2.0 cm in diameter. The Pt catalyst, in the form of a wire loop 0.025 cm in diameter and 3 cm long or a rectangular piece of foil $1.5 \times 0.3 \times 0.0025$ cm, was spot-welded at its ends to the leads of a glass-joint press-seal and suspended in the center of the glass tube. Platinum had a purity of at least 99.99%, and in separate experiments it was shown by Auger electron spectroscopy that specimens could be cleaned of all contaminants by heating to high temperatures in oxygen under similar conditions.

Temperatures were measured using Chromel–Alumel thermocouples spot-welded to the catalyst and also optically using a photomultiplier to measure emission from the surface. Temperature fluctuations were recorded on a strip chart recorder with a typical sensitivity of ±0.2°C and a response speed less than ~1 sec.

High-purity tank gases (99.99% NH_3 and 99.9% air) were used without further purification. Gases were mixed in a 60-cm-long tube filled with glass beads, and different mixing conditions were used to assure that incomplete mixing or flow variations did not influence results. In all experiments except those where the effect of changing the flow velocity was examined, the superficial air velocity based on the reactor diameter was held constant at 3.5 cm sec^{-1}. Thus the flow velocity of mixtures with up to ~40% NH_3 in air was in the range of 4 to 6 cm sec^{-1}. At these velocities, the gas flow through the system was laminar (the Reynolds numbers based on the tube diameter were <50).

Feed gas temperatures above ambient were attained by heating the inlet tube with Nichrome heating tapes. Wire and foil temperatures above the autothermal temperature pertinent to this reaction system were achieved by resistive heating. This form of heating was also used to ignite the reaction and to heat fresh wires or foils in a stream of air before igniting the reaction.

Observations were made on ~50 wires and 10 foils, each of which was used for 10 to 100 hr under varying conditions. Although data differed slightly between specimens, behavior was qualitatively similar throughout the experiments.

RESULTS

General Behavior

When reaction was initiated on a fresh wire or foil which had been heated resistively in air at ~900°C for a period of 1 hr, only steady states of the catalyst temperature were recorded at all mixture compositions, and for feed gas temperatures as high as 200°C. However, within 2–5 hr of reaction or within a shorter time of electrical heating to temperatures higher than the autothermal, oscillations were observed for certain operating conditions.

The overall NH_3 oxidation proceeds through two main reactions (*4*):

$$NH_3 + \tfrac{5}{4}\,O_2 \rightarrow NO + \tfrac{3}{2}\,H_2O \qquad (1)$$

$$NH_3 + \tfrac{3}{4}\,O_2 \rightarrow \tfrac{1}{2}\,N_2 + \tfrac{3}{2}\,H_2O \qquad (2)$$

which compete to form either nitric oxide or molecular nitrogen with stoichiometries of 14 and 21% NH_3 in air, respectively. These reactions are exothermic and the heat of reaction provides the so-called "adiabatic" catalyst temperature which is maximized near the stoichiometric point for oxidation to N_2.

In this work we monitored the "autothermal" catalyst temperature, i.e., the temperature resulting from the combined effects of heat generation by reaction and heat dissipation to the environment. All data will refer to these autothermal temperatures.

In all of our experiments with Pt wires and foils at all feed gas temperatures sustained oscillations were observed only in excess NH_3 (>21% NH_3 in air) and up to ~45% NH_3. This is indicated in Fig. 1 for a Pt wire exposed to various mixtures of ammonia and air at a gas temperature of

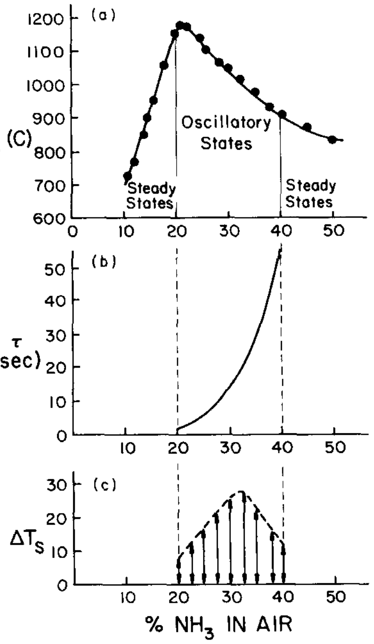

FIG. 1. (a) Average surface reaction temperatures on a 0.025-cm-diam Pt wire in NH_3 and air mixtures of 1 atm at T_g = 120°C for flow velocities of 4–7 cm sec^{-1} (measured at 25°C). (b) and (c) Periods and amplitudes of oscillations in the 20–40% NH_3 in air range for same conditions as in (a).

120°C and flow velocities of 4–7 cm sec^{-1} (measured at 25°C). Higher flow velocities produced similar behavior. As shown in Figs. 1b and c, an increase in the period of oscillation was observed as the NH_3 content of the mixtures was increased, while the amplitude of oscillations went through a maximum. In general, oscillations had amplitudes up to 50°C with periods from 2 to 200 sec.

Typical strip chart recorder traces of temperature versus time are shown in Fig. 2 for two different wires but with roughly comparable gas temperatures and flow velocities. These data illustrate the typical reproducibility between different wires.

While foils were not examined as extensively as wires, behavior was qualitatively similar. Oscillations occurred at roughly the same composition range as for wires, but on foils the frequency of oscillations was generally higher and patterns more commonly exhibited multiple peaks. Figure 3 shows typical traces of the temperature of a Pt foil exposed to a feed gas containing 37% NH_3 in air at 25°C.

Variation of Gas Temperature

As the feed gas temperature was increased, oscillations generally had higher frequency and amplitude. Also, the range of oscillation-inducing mixtures (Fig. 1a) extended to higher NH_3 concentrations at higher gas temperatures.

From results on several wires, the general behavior observed versus gas composition is shown in Fig. 4 for gas temperatures T_g up to 400°C with all wire temperatures autothermal. For gas temperatures less than 60°C steady states were observed for all compositions. However, simple periodic oscillations occurred if the catalyst had previously been at higher T_g for prolonged times. For gas temperatures from 70 to 170°C, single and multipeak periodic oscillations occur as shown in Fig. 2.

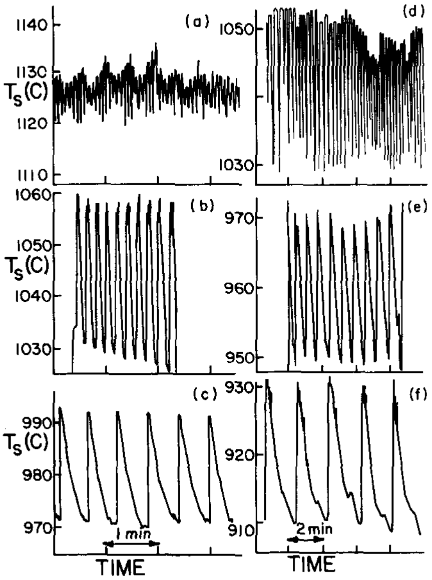

FIG. 2. (a) through (c) show examples of periodic catalyst temperature states for a 0.025-cm-diam Pt wire at T_g = 120°C. (a) 25%, (b) 30%, and (c) 33% NH_3 in air mixtures. (d) through (f) show periodic states on another Pt wire at T_g = 150°C. (d) 30%, (e) 36%, and (f) 38% NH_3 in air.

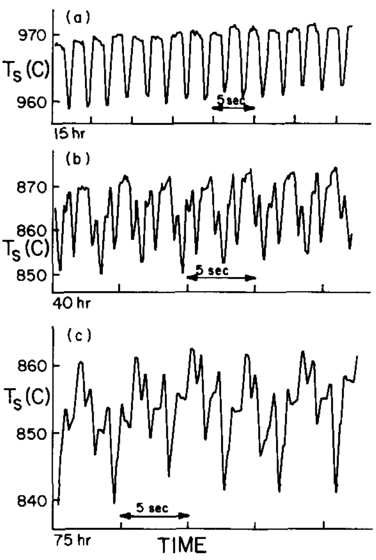

FIG. 3. Temperature of a Pt foil exposed to a 37% NH_3 in air mixture at T_g = 25°C.

Above ~170°C, patterns become more complex and large negative (cooling) spikes of 20 to 100°C amplitude occur. Figure 5 shows four typical patterns for increasing T_g. At 200°C and 40% NH_3 in air (Fig. 5a) a periodic negative spike with a period of ~20 sec occurs, while at 210°C and 32% NH_3 (Fig. 5b), a complex and nearly periodic pattern is observed. At 235°C and 33% NH_3 (Fig. 5c), the spikes appear more random, while at 280°C (Fig. 5d), regular multiple spikes with occasional spikes of larger amplitude occur. Boundaries separating one region from the other in Fig. 4 are not always well defined. As will be discussed later, the evolution of patterns with time, the pretreatment history, and the apparent "memory" of the catalyst seem to be important parameters affecting the dynamic behavior of the system.

As T_g is increased to ~280°C, apparent steady states are observed for all compositions. These are accompanied by noise (spikes of high frequency and small amplitude for which the recorder cannot respond rapidly enough). Frequently, these steady states are interrupted at irregular intervals by large negative spikes as shown in Fig. 6a for a mixture with 45% NH_3 in air at T_g = 290°C.

Finally, at temperatures above ~330°C and in excess NH_3, a regular pattern of large oscillations begins. This is associated with the homogeneous gas-phase reaction as confirmed visually by the propagation of a yellow flame from the wire back to the mixing point, which creates a periodic ignition and extinction of the reaction on the wire. In Fig. 6b, oscillations with large amplitudes of ~600°C are recorded on a wire exposed to 30% NH_3 in air at T_g = 420°C. The wire cools because all oxygen is consumed (in excess NH_3) and then ignites when the unreacted gas mixture reaches it. A complex pattern of ignition on the wire is then noted which concludes by a positive spike as homogeneous reaction begins around the wire.

Transients

Figures 7a through c illustrate the transient behavior of the catalyst temperature upon changing reactant composition at the same T_g. Figure 7a shows a transient on a wire at T_g = 120°C which had been in a 36% NH_3 in air mixture for several hours. The new oscillatory pattern in 38% NH_3 was attained in ~3 min.

Longer transients are obtained upon larger perturbations of flow velocities, such as in going suddenly from a steady state in the excess O_2 region to an oscillatory state

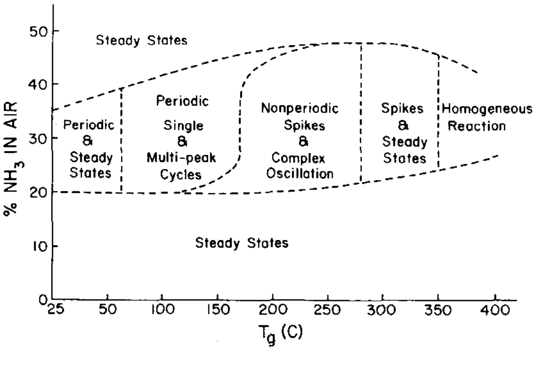

FIG. 4. Observations of dynamic behavior in NH_3 oxidation on Pt wires as functions of gas temperature and composition.

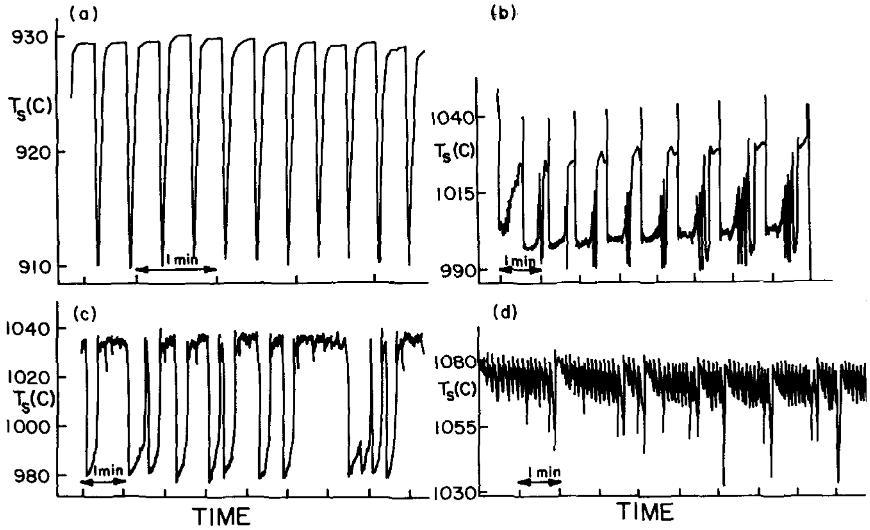

FIG. 5. Effects of gas temperature on oscillatory behavior: (a) 40% NH_3 in air at T_g = 200°C, (b) 32% NH_3 in air at T_g = 210°C, (c) 33% NH_3 in air at T_g = 235°C, and (d) 30% NH_3 in air at T_g = 280°C.

in excess NH_3 or vice versa. An example of this is shown in Fig. 7b for a change of gas composition from 16 to 25% NH_3 at T_g = 25°C.

Similar transient behavior was found in foil temperatures. In Fig. 7c, step changes in composition were made from 20 to 25 to 21% NH_3 in air so that, upon equilibration, oscillations should only occur at 25% NH_3. The average temperature attained its new value within 5 sec, which indicates that the gas composition attains steady state within this time. However, the oscillation pattern only approached steady state after ~20 sec and died after ~30 sec. In general, the temperature of the wire settles to a new average value upon changing the gas composition or flow rate much faster than does the pattern.

Evolution with Time

In several tests with different wires, all of the variables of the system were left unperturbed for many hours to examine the evolution of an oscillatory pattern with the time of reaction. The period and amplitude of oscillations usually increased slowly with

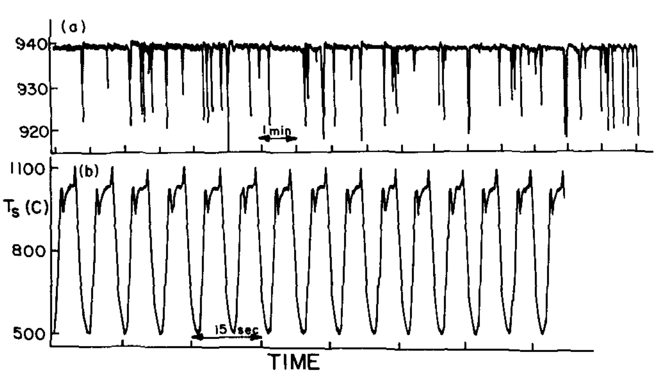

FIG. 6. (a) Nonperiodic spikes observed in a 45% NH_3 in air mixture at T_g × 290°C. (b) Periodic ignition and extinction of the reaction for a mixture of 30% NH_3 in air at T_g = 420°C.

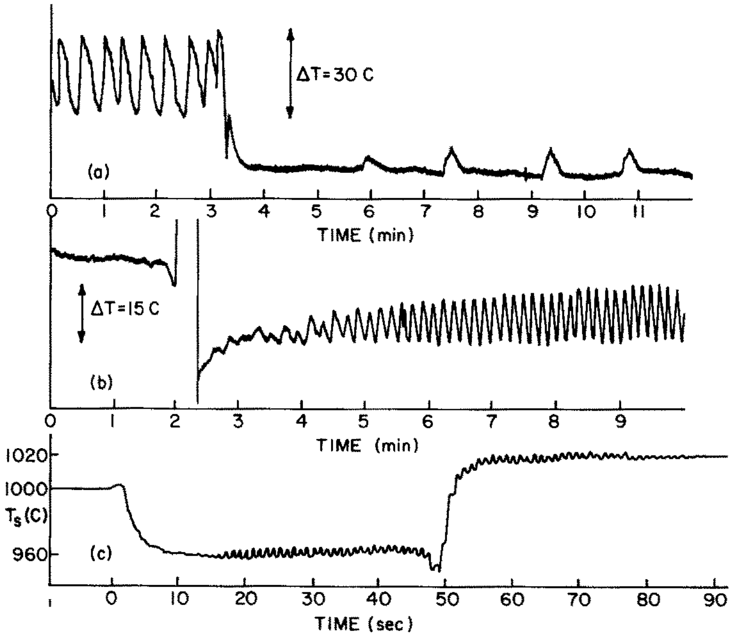

FIG. 7. (a) Transient on a Pt wire for a change in composition from 36 to 38% NH_3 in air at T_g = 120°C. (b) Transient on a wire upon changing composition from 16% (steady state) to 25% NH_3 in air at T_g = 25°C. (c) Transients of temperature of a Pt foil for perturbations in gas composition from 20 to 25 to 21% NH_3 in air at T_g = 25°C.

time and more complex patterns were obtained.

As shown in Fig. 8, multipeak "trains" of oscillations with varying frequency appeared for a 32% NH_3 mixture at T_g = 120°C. The initial pattern consists of over 30 peaks and has a period of ~5 min. Gradually, this oscillatory pattern became simpler in that fewer peaks occurred between periods, and finally, after 4 hr, simple cycles of some intermediate frequency developed. We observed that if both reactants were turned off at some point during the evolution of such a complex pattern, upon starting the reaction again after a few hours, the same oscillatory pattern continued, that is, cooling alone did not "erase" the catalyst "memory." However, if the Pt wire was removed from the reactor and allowed to reach equilibrium with laboratory air, the pattern was usually different, and frequently only steady states were observed.

It is interesting to note that when steady states existed in the usual oscillatory regime, heating the catalyst resistively in pure NH_3 to 800–1000°C for 1–2 hr would restore the oscillatory behavior. The same effect could be produced without electrical heating if pure NH_3 at $T_g > 150$°C was allowed to flow through the system for about 8 hr.

Other observations were made in connection with the resistive heating of the wires to higher than the autothermal temperatures. Generally, if resistive heating was imposed for short times (10–15 min) during some developed oscillatory state, it would not permanently affect the pattern. Long treatments of a few hours, however, would invariably change the pattern, and the "memory" of the higher-temperature behavior was retained for hours. Still, no sustained oscillations could be obtained in excess O_2 by this procedure.

DISCUSSION

This is obviously an extremely compli-

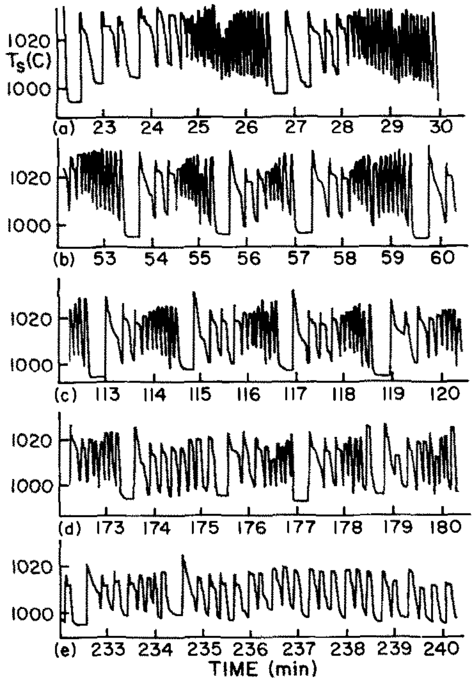

FIG. 8. Evolution of an oscillatory state for a 32% NH_3 in air mixture at T_g = 120°C. Times indicates refer to this particular run.

cated reaction system, and it is clearly not a good candidate for detailed modeling. However, the system is a rather simple one to characterize experimentally because the geometry is simple, and variables can be manipulated over wide ranges. Also, since the oscillation frequencies are higher than those reported for H_2 and CO oxidations, it is experimentally possible to observe many more cycles during a given period of time.

Comparison with Other Oscillatory Catalytic Reaction Systems

There is a remarkable similarity between much of the behavior reported here and behavior summarized by Sheintuch and Schmitz (*1*) for the other oscillatory catalytic reaction systems found to date even though they operate under quite different conditions. In most systems, oscillations exhibit single-peak cycles (*5–10*), usually of the relaxation type (*11, 12*). Complex periodic cycles with a number of peaks on a single cycle such as those observed here have also been found in the oxidation of H_2 (*5, 6, 12, 13*) and CO (*5–7, 11, 14*). Hugo (*15*) noted irregular pulses or spikes in N_2O decomposition, just as observed in this system for high gas temperatures. In all systems oscillations occur only over a limited range of compositions, and frequencies and amplitudes are composition dependent.

Some patterns observed here appear to consist of random peaks or of regular peaks with random perturbations superimposed. Truly nonperiodic oscillations (chaos) have been proposed for H_2 oxidation on Ni (*13*), but, while we observe oscillations of comparable complexity, the slow evolution of patterns makes it impossible to decide experimentally whether oscillations are truly nonperiodic.

Many previous experiments on oscillations employed stirred tank reactor geometries, and periods of oscillations were frequently equal to or longer than the reactor residence time. In our experiments the equivalent residence time, roughly the surface dimension divided by the flow velocity, was much less than 1 sec. Oscillations with periods from about 1 sec to several minutes were observed. Thus, while frequencies are generally higher here, they are comparable or longer multiples of reactor residence times.

Changes in the nature of oscillations and effects of catalyst pretreatment and time of reaction on the oscillatory behavior have bene noted in much of the previous work (*1, 12, 13*), as well as here, and have been attributed to changes in catalyst activity. With the Pt wires and foils used in our experiments, results were qualitatively comparable for any pretreatment after a few minutes of operation. A major factor affecting initial activity on platinum is almost certainly carbon, which is known to be oxidized by heating to high temperatures in oxygen.

Factors Other than Surface Phenomena

The main reactions that describe the

complex ammonia oxidation system are sufficiently fast and exothermic that at a total pressure of 1 atm the overall reaction is essentially mass transfer limited on either side of the stoichiometric ratio (21% NH_3 in air). Mass and heat transfer to and from the catalyst surface take place simultaneously with the surface reaction and large temperature and concentration gradients exist between the surface and the flowing gas stream.

During nonisothermal operation, kinetic instabilities may be amplified by thermal effects. However, as was shown by Ray *et al.* (*16*), thermal instabilities alone do not predict any periodic phenomena on catalytic wires in uniform, time-invariant external concentration and temperature fields.

Forced and natural convection could produce oscillations in flow and, consequently, in reactant concentration and surface temperature. The Reynolds numbers in these experiments were typically much less than those required for the onset of turbulence. However, the geometry of the suspended catalyst, thermocouple, and metal leads does not rule out the possibility of wakes and eddies downstream of the catalyst. The large temperature gradient in the boundary layer may induce natural convection. In fact, the sensitivity of oscillations to the orientation of the reactor suggests that natural convection is significant. However, convection effects should have time scales shorter than the typical periods of oscillations observed and, therefore, it seems improbable that convection alone can explain all features of the sustained oscillations in NH_3 oxidation.

The homogeneous gas-phase reaction is certainly the cause of oscillations at sufficiently high gas temperatures ($T_g >$ 300°C) because a periodic flame is produced. Also, the regular or random spikes observed at gas temperatures below the onset of stable flames may be associated with homogeneous reaction on a microscopic level. Evidently, at lower temperatures the homogeneous reaction propagates in the hot gas of the boundary layer (and perhaps downstream) but the flame is extinguished in the colder reactant gas.

Surface Reaction Influences

While heat and mass transfer, convection, and homogeneous reaction may all be significant in these experiments, most of the observed oscillatory behavior clearly indicates the importance of chemical rate processes.

Sustained oscillations were only produced in NH_3-rich mixtures, and heating the catalyst in pure NH_3 (but not air) was found to restore the oscillatory behavior. These effects argue in favor of certain chemical processes such as the reduction of the metal and the chemisorption of reactants. In fact, at high temperatures and in excess NH_3, the endothermic decomposition reaction, $NH_3 \rightarrow \frac{1}{2} N_2 + \frac{3}{2} H_2$, can occur, and, if oxidation of hydrogen were not instantaneous, the coupling of exothermic and endothermic surface reactions could lead to oscillations.

The importance of the treatment history of the catalyst, the evolution of patterns with time, and the long retained "memory" of exposure to high temperatures manifest the existence of slow surface processes, which gradually change the state of the catalyst.

These changes can be both chemical and morphological (catalytic etching). Experiments have shown (*17*) that this reaction produces faceting and pitting of initially smooth Pt surfaces on a time scale of minutes to hours. The size of these structures (1–10 μm) is sufficiently small that the overall boundary layer is unaffected, but a large increase in surface area occurs. The morphology depends on gas composition and surface temperature, and morphologies can be reversed over time scales of many minutes by changing these variables (*18*). Note, however, that morphology changes should produce only subtle changes in the process because, being mass transfer limited, the overall reaction is not significantly affected by the surface area.

The chemical composition of the catalyst surface should also change slowly with time. At 1 atm, 15 to 30 min are required to burn off the carbon layer initially present on Pt. While we have shown by Auger electron spectroscopy that Pt surfaces are free of gross contamination in this reaction under comparable operating conditions, a multilayer surface oxide probably forms in excess O_2 at a pressure of 1 atm. The presence of this oxide may inhibit oscillations. Thus, we suggest that slow changes in the chemical composition of the catalyst are more likely to produce oscillatory behavior than morphological changes. In fact, in excess O_2 where only stable steady states occur, catalytic etching was found to take place at a higher rate (*18*) than in excess NH_3. This also argues that chemical surface changes are more important than morphological ones in explaining oscillations.

SUMMARY

Experiments with ammonia oxidation on platinum wires and foils have revealed stable steady states, sustained periodic states, and also states with a complex oscillatory character.

We have examined more variables and have studied the reproducibility and time evolution of oscillations for this reaction more extensively than has been possible for the other surface reactions which produce oscillations. Although this reaction system is clearly the most complicated of those thus far studied and its oscillatory behavior was examined under mass-transfer-limiting conditions, the similarities with other systems suggest that comparable mechanisms may be operating in all systems.

Homogeneous reaction was found to be responsible for the oscillations at high gas temperatures. It was also suggested that an interplay between the endothermic decomposition and the exothermic oxidation reactions may cause oscillations in excess NH_3.

Transients demonstrate "memory" effects and show that this system retains characteristics of previous conditions after gas composition and surface temperature have established new steady-state values. Transients thus indicate that slow surface changes are important in oscillations, and such measurements appear to provide an important means of characterizing the nature of oscillations.

While much of the observed oscillatory behavior appears to be characteristic of the surface, no unequivocal explanations can as yet be offered, because of the seemingly important physical processes that also occur in this and perhaps most of the previous experiments. Since the kinetics of ammonia oxidation or of the other oscillatory reaction systems studied to date are not known, it cannot be decided whether or not the coupling between chemical and physical processes is necessary for the appearance of oscillations. Clearly, experiments under completely isothermal conditions and free of flow effects are needed in order to eliminate physical transport. Experimental work along these lines is currently in progress.

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