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NOTES

Dilution Effects in the Dynamics of Ammonia Oxidation on Platinum with an Inert or a Product Species in the Feed Mixture[1]

INTRODUCTION

Simple and complex periodic oscillations in catalyst temperature and reaction rate have been observed during the oxidations of hydrogen (*1–9*), carbon monoxide (*4, 5, 9–16*), and cyclohexane (*17*), and the reactions between NO and CO (*18*), NO_2 and CO (*19*), and between NO and NH_3 (*20*). Comprehensive reviews of the literature have been presented by Sheintuch and Schmitz (*14*) and Slinko and Slinko (*21*).

Low temperature hydrogen and carbon monoxide oxidations are perhaps the simplest systems because they presumably involve a small number of intermediates and are isothermal, but even for these reaction systems no unique explanation has as yet been given for oscillations.

Ammonia oxidation proceeds via two main overall reactions,

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (1)$$

and

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (2)$$

which compete to form either nitric oxide or molecular nitrogen, with stoichiometries of 14.3 and 21.8% NH_3 in the mixture of ammonia and air, respectively. Both reaction Eqs. (1) and (2) are exothermic with the heats of reaction

$$\Delta H(1)298°\text{K} = -54.1 \text{ kcal/mole } NH_3 \qquad (1a)$$

and

$$\Delta H(2)298°\text{K} = -75.7 \text{ kcal/mole } NH_3 \qquad (2a)$$

so that the maximum adiabatic catalyst temperature occurs at the stoichiometric mixture corresponding to Eq. (2). There has been one report, so far, on oscillatory states during the ammonia oxidation by air on Pt (*22*). In that study (*22, 23*), oscillatory behavior has been observed in excess of NH_3 in the feed mixture, and periods less than 50 s have been reported. The cause for those oscillatory states was attributed to the kinetics and possibly to physical phenomena.

The purpose of this paper is to show that homogeneous reaction, convection, and heat and mass transfer play the essential role in the oscillations observed in the oxidation of NH_3 on Pt.

EXPERIMENTAL

Three different reactors were used. One of them was exactly the same as the one described by Stephanopoulos (*23*). The second was similar to the previous reactor but without the Pyrex window 25 mm ϕ. The third was modeled after that used by Schmitz *et al.* (*24*). The catalyst was a high purity (99.99%), 0.025 cm diameter Pt wire, 2.5 to 7 cm long, and its ends were spot-welded to the nickel leads of a glass-joint press-seal.

Temperatures were measured by a Chromel–Alumel thermocouple spot-welded to the center of the wire. The wire temperatures measured were calibrated periodically with an optical pyrometer. Chromel and Alumel wires 0.0025 cm in diameter were used in the thermocouple. In all, 12 wires were used, 4 in each reactor, for 8 to 40 h under varying conditions. Temperature was recorded on a strip chart recorder with a typical sensitivity of ±0.2°C and a response speed less than 0.5 s. For different wires, different pretreatment procedures were em-

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ployed. Six of the Pt wires were heated to 900 to 1200°C for 30 to 150 min in air at atmospheric pressure, two of them were heated to 900°C in NH_3 for 1 h, and the remaining four were used with no treatment at all.

High purity gases (99.9% NH_3, 99.9% air, and 99.9% N_2) were used without further purification. Gases were mixed first in a 30-cm-long tube filled with 3-mm glass beads and then in a 50-cm-long tube filled with a mixture of 3- and 4-mm glass beads (*25*). Different mixing modes were employed to assure that incomplete mixing or flow variations did not influence our results.

The gas phase temperature was varied between 20 and 300°C by heating the inlet tube and the reactor with Nichrome heating tapes for temperatures above ambient. The catalyst temperature was kept in the range 500 to 1200°C by resistive heating for temperatures above the autothermal ones. This form of heating was also used to ignite the reaction and to pretreat the catalytic wires in a stream of air before igniting the reaction. The reactor pressure was 1 atm; the flow rates of each species at standard conditions (0°C, 760 mm Hg) were between 1 and 6 cm^3/s for NH_3, 3 and 10 cm^3/s for air, and 0 and 17 cm^3/s for N_2; and the feed stream NH_3 composition was varied between 8 and 55%. The superficial linear gas velocity through the reactor was 1.5 to 9 cm/s, and Reynolds numbers based on the tube diameter were between 15 and 100. The gas flow through the reactor was laminar, because in most experiments the Reynolds numbers did not exceed 60.

Although data differed from wire to wire and from reactor to reactor, behavior was qualitatively similar throughout the experiments.

RESULTS

In most experiments we monitored the autothermal catalyst temperature, i.e., the temperature resulting from the combined effects of heat dissipation to the environment and heat generation by reaction.

The temperature oscillations observed in the reactor modeled after Schmitz *et al.* (*24*) were more complicated than those observed in the other two reactors, and their amplitude was larger by a factor of 1.5 to 2.0 than one of the oscillations in the other reactors. However, the oscillatory behavior observed in these three different reactors was qualitatively the same. More details have been reported in (*25*).

In Fig. 1 the amplitude and the period of the catalyst temperature oscillations are shown versus the composition of NH_3 in the feed mixture. The NH_3 composition starts from 29.4% NH_3 in a mixture of NH_3 and air, and ends to 12% NH_3 in a mixture of NH_3, air, and nitrogen. At the one end of this plot, 29.4% NH_3, the temperature amplitude of the oscillations is 50°C and their period is 3 s. At the other end, 12% NH_3, the amplitude becomes 2°C and the period 240 s. Further addition of N_2 yields a steady state. Note that the amplitude, wave form, and period of the catalyst temperature oscillations are reproducible for increasing or decreasing amounts of N_2 in the

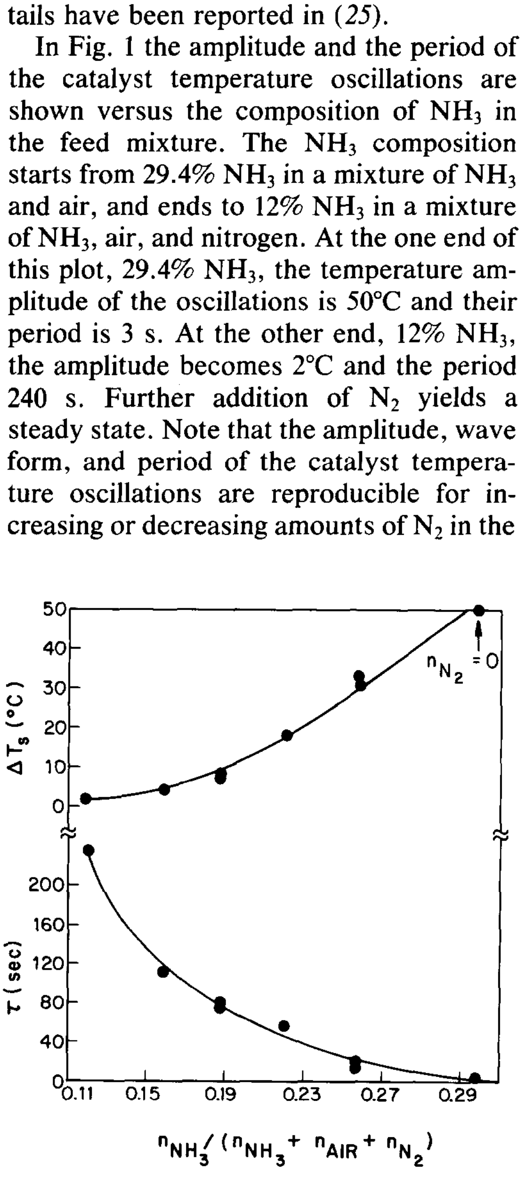

FIG. 1. Periods and amplitudes of Pt temperature oscillations in excess of nitrogen, at 1 atm, T_g = 135°C and flow rate 23.7 cm^3/s (at standard conditions).

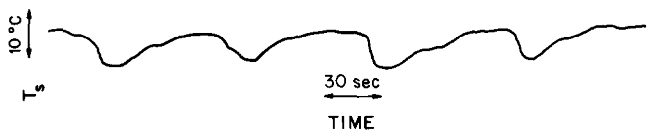

FIG. 2. Temperature of a Pt wire, 3.5 cm long vs time at T_g = 135°C, 4.2 cm³/s NH_3, 10 cm³/s air, and 9.5 cm³/s N_2.

feed mixture. In all NH_3 compositions between 12 and 29.4%, the catalyst temperature oscillations are single peaked, an example of which is presented in Fig. 2. In this figure, raw data of N_2 dilution effects are shown at a composition 17.7% NH_3. Single peaked oscillations emerge in 1 to 2 min, with an amplitude of 10°C and a period of 75 to 80 s.

Whenever NH_3 and air only were used as the feed gases in our system, we observed oscillations for NH_3 compositions between 12 and 45%, with periods of less than 25 to 30 s and wave forms ranging from single peaked to very complex and nonperiodic.

In Fig. 3, the temperature is presented with respect to time at a feed concentration 23% NH_3, 75% air, and 2% water vapor which is one of the products of NH_3 oxidation, on a platinum wire 3.8 cm long. This response is nonperiodic. In two runs on two different wires the reaction was run for 12 h continuously at the feed gas stream composition mentioned above, and the recorded response was nonperiodic (25). The nonperiodic response of our system in the presence of small amounts of water was observed in all three reactors, on five different platinum wires, and disappeared within 2 min when addition of water in the feed stream was stopped.

In a few runs, the system was left unperturbed for many hours to examine the evolution of an oscillatory pattern with respect to the time of the reaction. Reproducibility was also studied. In Fig. 4, a feed mixture containing 23% NH_3 and 77% air, at a gas phase temperature 150°C and a total volumetric flow rate 605 cm³/min was used in order to study such evolution and reproducibility effects. First, we observed catalyst temperature oscillations of a period of 3 s and an amplitude of 12°C (Fig. 4a). One hour later the same pattern persisted (Fig. 4b). Then, the operating conditions of this run were changed for the next 2 h; when the run came back to the conditions we began with, the pattern shown in Fig. 4c was obtained. For the following 2 h, the reaction was run continuously at different operating

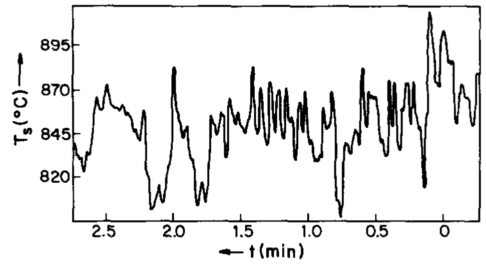

FIG. 3. Pt wire temperature vs time at T_g = 30°C and a flow rate 565 cm³/min. Here, 23% NH_3, 75% air, and 2% water vapor. Pt catalyst is in its 15th h of operation and 3.8 cm long.

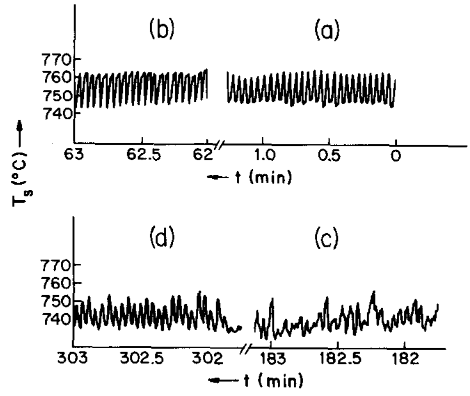

FIG. 4. Reproducibility and evolution of Pt temperature with respect to time. T_g = 150°C, 23% NH_3, 77% air, and a total flow rate 605 cm³/min. Pt wire is in its 12th h of operation (at t = 0) and is 3.6 cm long.

conditions, and when it was brought back to its initial state, the pattern of the temperature oscillations shown in Fig. 4d was obtained. In this case, reproducibility of our results is within ± 15%, because the period and the amplitude of the oscillations obtained in Fig. 4d are the same as those attained 5 h before.

DISCUSSION

Ammonia oxidation is a complicated reaction system and thus not a good candidate for detailed modelling. In addition, at a total pressure of 1 atm, the overall reaction is mass-transfer limited on either side of the stoichiometric ratio toward nitrogen (21.8% NH_3 in the feed mixture). However, this system is simple to characterize experimentally because its geometry is simple and variables can be manipulated over wide ranges.

M. Stephanopoulos *et al.* (*22*) reported catalyst temperature oscillations of a simple or complex form during the oxidation of NH_3 by air, with periods less than 50 s and amplitudes less than 30°C. In our studies, under similar conditions, periods greater than 25 s were rarely observed, while the amplitude of the oscillation was greater than the one reported in (*22*) by a factor of 2. In (*22*), oscillations were reported for NH_3 compositions between 21 and 45% in the feed stream, whereas in our experiments, oscillatory behavior was observed for NH_3 compositions in the range 12 to 45%.

In this system, we propose the following mechanism for the oscillations observed: when this heterogeneous chemical reaction occurs on a Pt wire or foil surface, the high exothermicity raises the temperature of the vicinity of the Pt wire or foil surface, thus promoting homogeneous reaction; this homogeneous reaction may subsequently starve the Pt surface of reactants leading to a lower temperature and thus "quenching" the homogeneous reaction (i.e., virtually zero rate) so that the Pt surface receives again more reactants; this oscillatory phenomenon combined with heat and mass transfer, convection, and "memory" effects of Pt surfaces may lead to the simple periodic, complex and nonperiodic oscillations observed. At higher nitrogen gas phase concentrations heat and mass transfer as well as convection may become less important, and the homogeneous heterogeneous mechanism mainly appears to drive the surface oscillations. Hence, the catalyst temperature oscillations are now always single-peaked and their amplitude decreases as the nitrogen gas phase concentration increases (Fig. 1).

The addition of small amounts of a product species, water vapor in this case, in the feed gas during the oxidation of NH_3 by air led to nonperiodic temperature oscillation at all times. This is consistent with the mechanism of oscillations presented before. However, there is no apparent reason why nonperiodic temperature oscillations are observed at all times in these experiments.

SUMMARY

Experimental studies on NH_3 oxidation by air over Pt wires have revealed stable steady states, sustained periodic oscillations and nonperiodic states. An excess of N_2 in the feed gas stream leads to simpler single-peaked catalyst temperature oscillations of increasing periods of up to 5 min. Small amounts of water vapor produced nonperiodic states at all times. Both of these indicate that an interplay of heat and mass transfer, convection, and a heterogeneous homogeneous mechanism is the cause of the intriguing phenomena observed during the oxidation of NH_3 by air on Pt, at atmospheric pressure. Catalyst "memory" effects may also contribute to these phenomena.

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