Reaction between Nitric Oxide and Ammonia on Polycrystalline Platinum. 2. Rate Oscillations

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Sustained reaction rate oscillations were observed during the reduction of nitric oxide by ammonia over polycrystalline wires at pressures between 0.2 and 1.0 torr, temperatures between 360 and 550 °C, and feed gas concentrations P_{NO}/P_{NH_3} of 1.5–4.0. Single-, double-, and triple-peaked oscillations with periods between 15 s and 5 min were observed. These oscillations were strongly dependent on the surface temperature, feed gas composition, and total pressure, although oscillatory behavior was stable over long periods of time. Qualitatively similar behavior was observed in adiabatic operation ($\Delta T_S \sim 100$ °C) using constant power input or with the wire temperature held constant. Because oscillations arise isothermally under conditions where transport limitations are absent and the catalyst surface is clean and remains unchanged morphologically, they must be caused mainly by the kinetics of the reactions. The model used to describe steady-state kinetics can also predict oscillations in this system although no quantitative model for this behavior is proposed.

Introduction

Periodic oscillations occur in the rates of several catalytic reactions such as the oxidations of hydrogen,[1-10] carbon monoxide,[4,5,9,11-17] ethylene,[18] and ammonia.[19] Comprehensive reviews of this literature have been presented by Scheintuch and Schmitz[15] and Slinko and Slinko.[20]

Among suggestions for possible causes of such a behavior are a shift between two states of the adsorbed reactant,[5,11] fluctuations in surface temperature,[21] dependence of the reaction rate constants on surface coverage,[2,3,15,22,23] requirement of empty sites in the reaction step,[24,25] dependence of heat of absorption on surface coverage,[27] a change in reaction mechanism with surface coverage,[12,13] oscillations in the concentration of an adsorbed inactive species,[28-31] changes in the state of a surface oxide,[10] phase transitions on the catalyst surface,[32] coupling between reaction kinetics and reactor mass balances,[31,33] and coupling between regions on a surface.[34,35] Unfortunately none of the existing models is capable of predicting quantitatively the experimental observations, and the causes of this behavior are not yet clear for any reaction system. Problems in interpreting most of the existing experimental studies are (i) boundary layer effects, (ii) poorly defined catalyst surfaces, and (iii) large time constants of the overall system compared to the periods of the oscillations observed.

Two recent experimental observations of oscillations at low pressures have also been reported, one in the reaction system NO_2 and CO[36] and the other for NO and CO.[37] The reaction between nitric oxide and carbon monoxide was studied by Adlhoch et al.[38] Their experiments were carried out at pressures of less than 5×10^{-4} torr and in the temperature range 440–520 K so that boundary layer effects were eliminated and the overall time constant was small compared to the periods of the rate oscillations observed.

An understanding of kinetics of oscillations should enhance the understanding of the rate processes occurring during catalysis and facilitate the discovery of reactions for which oscillations occur. This phenomenon may also be used for discrimination among rival kinetic mechanisms, since those which cannot predict oscillations are either oversimplified or wrong.[15,20] The final stage would be to use rate oscillations as a diagnostic tool in estimating pa-

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rameters of a system.

To our knowledge, this is the first report on concentration and/or temperature oscillations during the reduction of nitric oxide by ammonia on polycrystalline platinum. Oscillatory reaction rates were observed in the temperature range 360–550 °C and the only products formed in this region were molecular nitrogen and nitrous oxide. In our system, there are no boundary layer effects, no homogeneous reaction, and a fairly well-defined and reproducible surface. Detailed modeling of the dynamics of this system will be reported in a later publication.

Experimental Section

The apparatus and the procedure have been described previously.[39-41] The 380-cm^3 stainless-steel reactor was equipped with a differentially pumped quadrupole mass spectrometer. The background reactor was less than 0.002 torr,[40] and the high-purity NO and NH_3 reactants were purified as described[41] by passing through molecular sieve and charcoal traps. We examined the dynamics of this reaction system at three different total pressures, 0.2, 0.5, and 1.0 torr, at a gas-phase temperature equal to 25 °C and Pt wire temperatures between 360 and 550 °C. The catalyst was a 0.025-cm diameter, high-purity (matheson 99.99%) polycrystalline Pt wire 8–15 cm long (area $\approx$ 1 cm^2) whose temperature was measured with a Pt–13% Rh thermocouple. For the isothermal experiments, a minicomputer sensed the thermocouple readings and adjusted current through the wire using a programmable power supply to maintain the temperature constant to within ±5 K.

In a typical experiment, the wire was first cleaned by heating it to 1300 °C in oxygen at 0.015 torr for 15–20 min. Auger electron spectroscopy analysis of several wires after use showed that the surface was free of any contamination except carbon which presumably formed between times of reaction and surface analysis.

There has been discussion of morphological changes of the surface in theoretical[34] and experimental[35] studies which introduce a model incorporating morphological changes of a catalyst surface to explain temperature and rate oscillations. We examined several wires using SEM before and after use for many hours and found no significant increase in area or microstructures greater than 1000 Å in size (the resolution of SEM) except for occasional pits on the surface. Structural changes on a scale smaller than this wre not detectable. After the initial treatment of a new Pt wire, concentration and temperature oscillations appeared within the first few minutes of heating in an NH_3–NO mixture at the appropriate temperature. When present, oscillations usually appeared immediately, but, depending on previous temperature, steady states were sometimes observed initially which changed to oscillations within a few minutes.

The overall system time constant was always less than 7 s so that any dynamic phenomena with time constants greater than this would be clearly observed. The reproducibility of the rate and the current through the wire to maintain oscillations was reproducible to within ±10% with respect to period and ±15% with respect to amplitude. No systematic deviations with time or between different wires were ever observed.

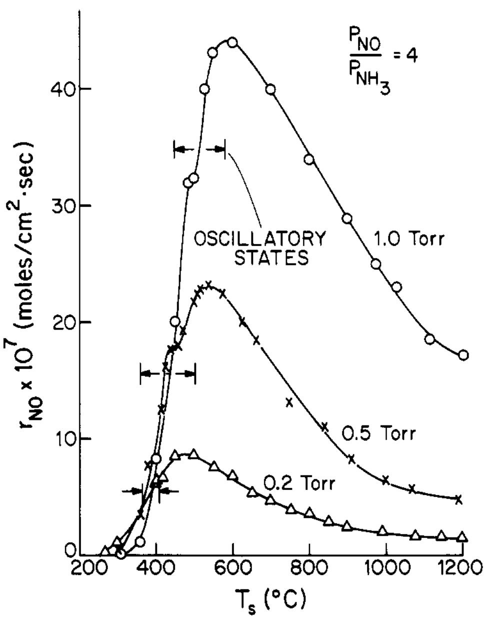

Figure 1. Regions of isothermal oscillatory states shown in a plot of NO consumption rate vs. Pt temperature for P_{NO}/P_{NH_3} = 4.

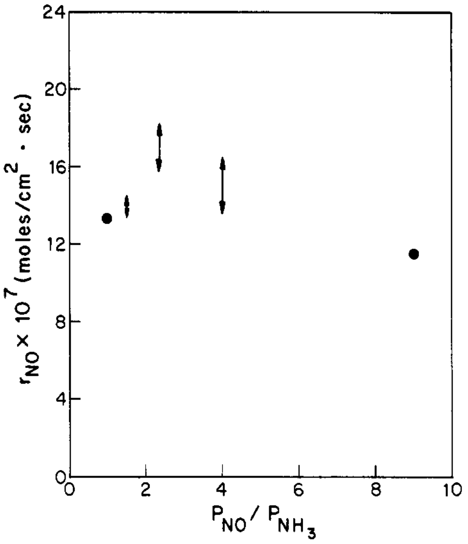

Figure 2. Isothermal NO consumption rate oscillations as a function of P_{NO}/P_{NH_3} at 425 °C and a total pressure of 0.5 torr.

Results

As discussed in the previous paper, the reaction between nitric oxide and ammonia proceeds at a measurable rate on polycrystalline Pt wires between 350 and 800 °C. In this paper we concentrate on the temperature range between 360 and 550 °C in which single-peaked and multipeaked oscillatory reaction rates are observed. Molecular nitrogen and nitrous oxide were the only products observed. The two overall chemical reactions which describe this system are

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \quad (1)$$

$$8NO + 2NH_3 \rightarrow 5N_2O + 3H_2O \quad (2)$$

with heats of reaction of 72 and 28 kcal/(mol of NO).

The range of gas-phase compositions from excess NH_3 (P_{NO}/P_{NH_3} = 1) to a large excess of NO (P_{NO}/P_{NH_3} = 9) was examined. Figure 1 shows the temperature range exhibiting isothermal oscillations for P_{NO}/P_{NH_3} = 4. Wire

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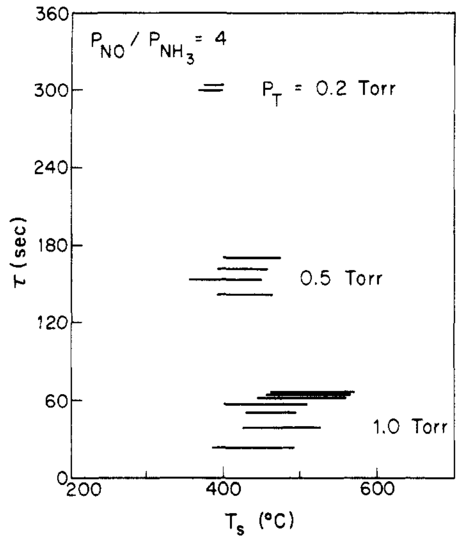

Figure 3. Periods and amplitudes of temperature oscillations as function of Pt temperature at several total pressures.

temperatures were maintained constant to within ±5 K during composition oscillations in these experiments. Figure 2 shows a plot of the composition ratios examined for isothermal oscillations at 0.5 torr and 425 °C. Concentration oscillations were observed only for compositions P_{NO}/P_{NH_3} between 1.5 (stoichiometric mixture for eq 1) and 4 (stoichiometric mixture of eq 2). Nonisothermal oscillations occurred over approximately the same range of compositions and temperatures.

In Figure 3, the sensitivity of the rate oscillations to total pressure variations is shown at a constant gas-phase composition ($P_{NO}/P_{NH_3} = 4$). In this figure the amplitude of the adiabatic temperature (constant wire heating current) oscillation is plotted vs. τ, the period of the concentration and temperature oscillations for pressures of 0.2, 0.5, and 1.0 torr. Three trends are evident from Figure 3. First, the temperature amplitude increases with total pressure. Second, when the total pressure increases by a factor of 5, the period of the oscillations decreases by a factor of 7–10. Third, increasing the reactor pressure from 0.2 to 1.0 torr increases the time-averaged temperature of oscillations by up to 120 °C.

In Figure 4 isothermal rate oscillations are shown at a gas-phase composition $P_{NO}/P_{NH_2} = 2.3$ and a total pressure of 0.5 torr. Oscillations were observed in the temperature range of 400–510 °C with an amplitude varying by a factor of 5 and a period varying by a factor of 7. These results indicate that the period and the amplitude of the oscillatory states are strongly dependent on the catalyst temperature.

In Figure 1 the NO consumption rate vs. catalyst temperature and the temperature range in which isothermal concentration oscillations occur are shown at a feed gas composition $P_{NO}/P_{NH_3} = 4$ at total pressures of 0.2, 0.5, and 1.0 torr. At all compositions and pressures the temperature ranges of oscillations always occur before the maximum of the NO composition rate is reached, where the coverages (fractions of saturation density) of the adsorbed species should sum to a number very close to unity. Also, these ranges always include the breaks in the average rate noted in the previous paper.

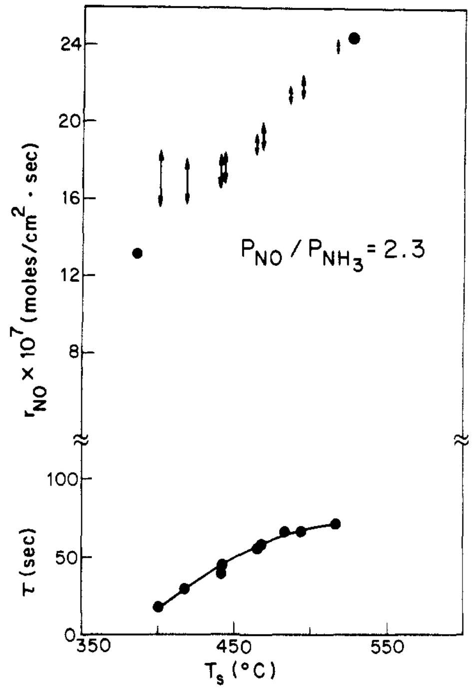

Figure 4. Periods and amplitudes of isothermal NO consumption rate oscillations as functions of Pt temperature for 30% NH_3 at a total pressure of 0.5 torr.

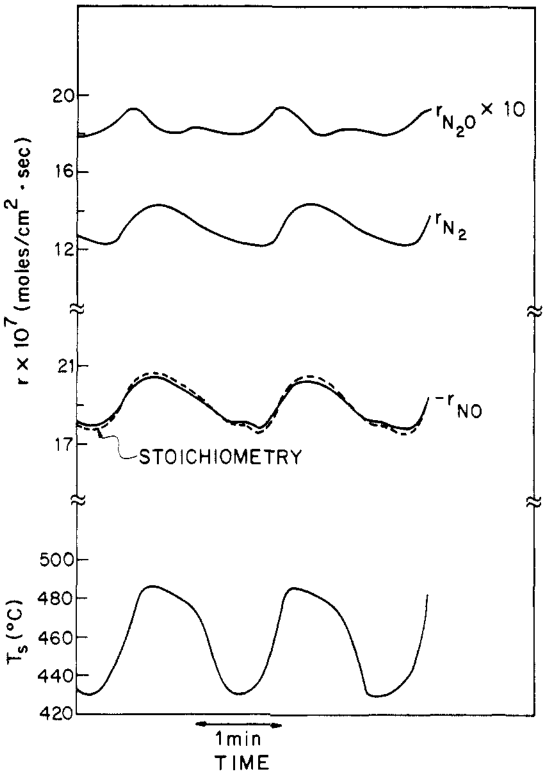

Figure 5. N_2 and N_2O formation rate, NO consumption rate, and Pt temperature oscillations in adiabatic reaction for $P_{NO}/P_{NH} = 4$.

Figure 5 shows typical plots of rates of N_2 and N_2O formation, NO consumption, and temperature vs. time over a two-period time interval. In each complete cycle, there exist two maxima in the N_2O formation rate, one before the maximum of the N_2 production rate and one after it. The catalyst temperature and the NO rate and the N_2 rate peaks are in phase, while the N_2O formation rate peaks lag the other peaks by 15 s.

In Figure 6 the rates of NO consumption, N_2 production, and N_2O formation are shown vs. time for P_{NO} = 0.4 torr and P_{NH_3} = 0.1 torr for isothermal oscillations at 432 °C. Two peaks of each species were observed in each cycle under these conditions and for all compositions under isothermal conditions. Using the stoichiometries of reactions 1 and 2, the N_2 and N_2O pressure changes predict NO pressure changes indicated by the dashed curve. This

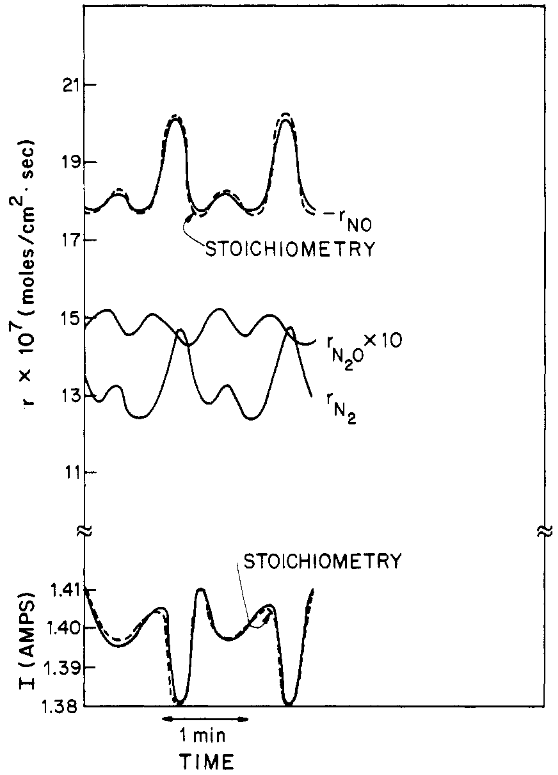

Figure 6. N_2 and N_2O formation rate, NO consumption rate, and current oscillations in isothermal reaction at 432 °C for $P_{NO}/P_{NH_3} = 4$.

shows that the mass balances are closed to within an experimental error of ±8%. In the lower part of this figure, the current through the Pt wire is shown as a function of time. From the amplitudes of the current oscillations and of the oscillating (consumption and formation) rates, and from the heats of reactions of eq 1 and 2, we calculate (dashed current curve) that the energy balance is closed within an error of ±10%. The current oscillation extrema are in phase with those of N_2 and NO with the qualitative difference that the maxima of these rates correspond to the minima of the current through the catalytic Pt wires as expected since both overall reactions are exothermic.

In qualitative experiments we found that addition of 0.5–1.5% acetone in a stoichiometric mixture of NO and NH_3 of 0.5 or 1.0 torr destroyed oscillations under conditions at which isothermal and nonisothermal oscillations occurred before. Although no systematic study of this phenomenon was attempted, the above result was reproducible as many times as we tried it. Several theoretical studies[28,31] have shown that the addition of a third species may lead to the existence of oscillatory states which are excluded otherwise[28,30] or to multipeaked oscillations.

We found that isothermal oscillations in a differential reactor exhibited a larger amplitude than that of the isothermal ones in a situation with higher conversions. In the case of nonisothermal variations, the periods were higher than at constant temperature by a factor up to 2.5, and double- or tripled-peaked oscillations were frequently observed. No chaotic (nonperiodic) behavior was ever observed.

Discussion

Several factors are known to enhance the likelihood of oscillatory behavior. Maintenance of the system far from equilibrium is essential for sustained oscillations.[28–30] Secondly, although complex feedback loops (i.e., autoinhibition) are not absolutely required, autocatalysis is found in many known chemical oscillators.[24] Finally, it has been suggested that many systems which exhibit bistability should be capable of oscillation when subjected to an appropriate feedback.[42]

The concentration and temperature oscillations (amplitude, wave form, and period) observed in the reaction between nitric oxide and ammonia over platinum wires are sensitive to the total pressure, composition of the feed gas stream, and catalyst temperature. At lower pressures, 0.2 torr, the amplitude of the rate oscillation is small (2–3% of the absolute rate) and its period increases to 5 min. At higher pressures, 1.0 torr, the amplitude of the oscillating rates increases to 18–20% of its absolute value, while the period becomes as small as 25 s. If the feed gas composition is changed in excesses of either NH_3 or NO, no oscillatory behavior is observed, whereas for compositions near and between the stoichiometric mixtures for reactions 1 and 2 oscillations are observed at all times. The amplitude and the period of these oscillations varied by a factor up to 8 when the catalyst temperature changed. Isothermal concentration oscillations are single- or double-peaked, while the adiabatic temperature and rate oscillations appear to be single-, double-, or triple-peaked.

Both physical and chemical causes have been suggested as explanations of rate oscillations. Most experimental studies have been carried out at high pressures so that mass transfer and boundary layer effects are important. Although it is typically suggested that chemical causes are largely responsible for most catalytic oscillations, it is difficult to extract quantitative information from most previous experiments. In our experiments, low pressures ensure no boundary layer or transport limitations.[43,44] Additional evidence for this is the fact that the maximum reaction probabilities obtained in our steady-state studies of this reaction system were between 0.02 and 0.04. Reaction probabilities obtained by Gland and Korchak[45] at pressures of 10^{-8} torr were also between 0.03 and 0.07.

Another possible explanation for rate oscillations is the "fuzzy-wire" model, in which protrusions on a catalyst play the key role. Recently, experiments carried out on Ni for the oxidation of hydrogen[35] were suggested to arise from that cause, although the high periods of those temperature oscillations are not satisfactorily explained by that model. SEM micrographs show that our Pt surfaces do not have macroscopic protrusions. Different pretreatments of the eight wires used were done by varying the time that they were exposed to oxygen from 1 to 5 h and by using different oxygen pressures from 0.010 to 1.0 torr. No qualitative differences were observed and all differences were less than ±15%, which is the experimental error of our data.[41]

Another suggested cause of oscillations has been a third species in the feed gas streams and/or on the catalyst surface. In our experiments AES characterization of wires after use showed no surface contamination.[41] The role of impurities in the feed gas stream was minimized by using continuous purification of the reactants, with dry ice–acetone cooled cold traps for condensables, molecular sieves, and activated charcoal. No differences were observed with or without the above purification treatments.

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The coupling between energy and mass balances of the reactor and the catalyst has also been shown to produce oscillations. Since most experiments were carried out at constant wire temperature and the gas was at room temperature, the influence of the energy balances is reduced and the possibility of homogeneous reaction taking place in the reactor[43] can be eliminated. Some of the experiments carried out in this work were at conversions up to 30% with respect to the limiting reactant. Under those conditions, along with the state of the catalytic surface and the adsorbed species, the reactor mass balances become important. Theoretical studies have been reported by Morton and Goodman[33] and by Chang and Aluko[31] which show that integral operation of a reactor may lead to oscillatory states of a small amplitude with one or three steady states even in cases where a differential reactor might lead to stable steady states. In most of our experiments the conversions were less than 8% with respect to the limiting reactant and the results were qualitatively similar to those with higher conversions, although quantitative differences were observed. These observations indicated that the operation of the reactor at higher conversion can couple with the surface reaction oscillations and lead to more complicated oscillation patterns but that this does not produce qualitatively different behavior.

The previous discussion indicates that the dominant cause for oscillatory states in this reaction system appears to be the surface reaction kinetics. Recent publications indicate that adsorbate phase transitions[32] or coverage-dependent rate parameters[22] may also lead to oscillatory behavior.

We shall report detailed modeling of this system in a future publication. In the previous paper we proposed the following mechanism for the reduction of the NO by NH_3:

$$NH_3 + 2S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NH_2\text{-}S + H\text{-}S \tag{3}$$

$$NO + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NO\text{-}S \tag{4}$$

$$NH_2\text{-}S + NO\text{-}S \xrightarrow{k_3} N_2 + 2S + H_2O \tag{5}$$

$$H\text{-}S + NO\text{-}S \xrightarrow{k_4} HNO\text{-}S + S \tag{6}$$

$$2HNO\text{-}S \xrightarrow{k_5} N_2O + H_2O + 2S \tag{7}$$

$$HNO\text{-}S + H\text{-}S \xrightarrow{k_6} N\text{-}S + H_2O + S \tag{8}$$

$$2N\text{-}S \xrightarrow{k_7} N_2 + 2S \tag{9}$$

No specific adsorbate-bonding configurations are implied by species indicated. Gland and Korchak[45] indicated that the two dominant adsorbed species on the Pt catalyst surface for the reaction between NO and NH_3 at pressures on the order of 10^{-8} torr are N–S and NO–S, where S stands for an empty site on the catalyst and surface, and N–S and NO–S stand for the adsorbed species of nitrogen and nitric oxide on Pt. Under our conditions, r_{N_2O} is significant so that θ_{HNO} cannot be negligible.

With the assumptions that (i) the reactor operates differently and (ii) reaction 3 reaches equilibrium very rapidly, we can write the mass balances for the adsorbed species NO–S, HNO–S, and N–S. It can be shown that these model equations exhibit oscillatory states for certain values of the parameters in that a single unstable solution to the three differential equations can exist.[49]

This model appears to describe this system accurately because (i) it predicts the steady-state nitrogen formation rate expression,[40] (ii) it predicts qualitatively the nitrous oxide formation rate,[40,41] (iii) it includes the surface complex intermediate as discussed by many investigators,[46–48] and (iv) it is consistent with the observation of rate oscillations. For multipeaked rate oscillations additional adsorbed species, coverage-dependent parameters, or phase transitions would have to be included. However, the above model includes the minimum number of rate parameters among the above choices.

Summary

Sustained oscillations occur in the reaction between nitric oxide and ammonia on polycrystalline Pt. These phenomena were strongly dependent on the catalyst temperature, feed gas stream composition, and total reactor pressure, and they were quantitatively reproducible on many wires, were independent of pretreatment conditions, and exhibited no transient or nonperiodic phenomena. Experimental conditions exclude any physical causes leading to oscillations, and we are left with the surface reaction kinetics of this system as the cause of catalytic oscillations. The mechanism proposed to explain steady-state kinetics is capable of predicting oscillations for particular values of parameters and assumptions about relative rates of various steps. However, it is not yet clear that this model is capable of predicting accurately the observed behavior for this system. Factors such as multiple adsorbate phases (probably of NO) or effects of microscopic surface phase changes may be necessary to explain these oscillations. These mechanisms will be examined in detail in future publications.

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