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Kinetics of NH_3 Oxidation on Pt, Rh, and Pd[1]

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The kinetics of the reactions involved in the catalytic oxidation of NH_3 have been studied as a function of temperature over polycrystalline Pt, Rh, and Pd wires in a steady state flow system using a differentially pumped mass spectrometer to monitor species concentrations. Unique and reproducible steady state rates were observed in all experiments for temperatures up to 1400°C at all compositions. Rates of individual reactions could be fit by Langmuir–Hinshelwood rate expressions with constant parameters, and comparisons of these parameters on different metals give reasonable qualitative interpretations for observed differences between metals. The competition of NO and NH_3 for adsorption sites appears to be important in determining the rates of various reactions. Differences in selectivity between metals are caused by the different temperature dependences of rates of individual reactions rather than by uniform differences in rates. Kinetics measured at low pressures (0.1–1 Torr) are used to estimate selectivities of NO and N_2 production at conditions of industrial nitric acid production. The predicted selectivity and optimum temperature and composition on Pt assuming simple models of flow patterns over the catalyst gauze match closely those observed in the high pressure process.

INTRODUCTION

Kinetics of catalytic reactions are seldom measured with a precision suitable for predictions of rates at conditions far from those of actual measurements. This is largely because of the uncertainties in determining active surface areas of catalysts and because of constraints on operating pressure and temperature set by system and catalyst stability and the need to avoid side reactions which may become important outside of the conditions studied. The lack of generality in rate expressions expressed as powers of concentration and an effective activation energy and preexponential factor frequently prohibits the testing of reaction mechanisms in more than a qualitative manner. Such expressions are also not suitable for scaleup to realistic operating conditions.

In this paper we examine the kinetics of the reactions involved in NH_3 oxidation on the transition metals Pt, Pd, and Rh between room temperature and temperatures near the melting points of the metals. Surfaces are polycrystalline wires which duplicate closely the wire gauzes used in the industrial processes. We shall fit data for all reactions to Langmuir–Hinshelwood (LH) rate expressions and show that such expressions give generally good agreement with data at all temperatures and gas compositions. The expressions obtained from measurements between 0.1 and 1.0 Torr will then be used to predict selectivities under high pressure conditions. A preliminary account of this work on Pt has been given previously (*1*). In the present paper rates are compared on all three metals, analysis with LH kinetics is extended to the simultaneous reactions in NH_3 oxidation, and scaleup is included.

Ammonia oxidation is an ideal prototype reaction for such studies because it in-

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volves relatively few species and stoichiometrically independent reactions and because the industrial reaction (to produce nitric acid) has been carried out for 50 yr under only slightly changing conditions (*2–4*). While operating conditions are well established and highly efficient (conversions and selectivity to NO approaching 99%), some questions of catalyst stability remain (*2*).

The reaction between NH_3 and O_2 produces some N_2O at low temperatures, but above 400°C the only nitrogen containing species observed were NO and N_2. In measurements at a total pressure of 1 atm Andrussow and Bodenstein (*5*) reported traces of NH_2OH, but recent kinetic studies confirm the absence of other than the above products except in trace amounts. The older mechanisms for this reaction which involve hydroxylamine or imide intermediates cannot be tested (*5–7*), but from more recent experiments (*8,9*) it has been suggested that N_2 production at low temperatures can be interpreted more simply as a bimolecular reaction between NO and NH_3 to produce N_2. However at high temperatures the unimolecular decompositions of NH_3 and NO also produce N_2. Thus one can write the reactions formally as

$$NH_3 + O_2 \rightarrow NO + H_2O, \qquad (1)$$

$$NH_3 + NO \rightarrow N_2 + H_2O, \qquad (2)$$

$$NH_3 \rightarrow N_2 + H_2, \qquad (3)$$

and

$$NO \rightarrow N_2 + O_2, \qquad (4)$$

Reaction (1) produces, NO, and reactions (2) and (4) represent series processes leading to N_2 through NO intermediates, and reaction (3) a parallel process (not involving NO) leading to N_2.

These are the only reactions necessary to describe the nitrogen containing products except for N_2O. We assume that H_2 from reaction (3) would be quickly oxidized to H_2O in the presence of O_2, but we did not examine the hydrogen containing species in detail. The objective of our work is to describe the kinetics of the above reactions by measuring rates of N_2 and NO production with various mixtures of NH_3, O_2 and NO. We shall show that our results agree with the suggestion of Fogel *et al.* (*8*) that the series process, reactions (1) and (2), adequately describes the production of N_2 for temperatures below 1200°K and at pressures above 0.1 Torr. However, we shall not speculate on reaction "mechanisms" (specification of adsorbed intermediate species) except as they are implied by measured kinetics.

EXPERIMENTAL METHODS

The apparatus and procedure have been described previously (*1,10,11*). Gases were passed over heated 0.010 in. diameter high purity (>99.9%) wires in a Pyrex flow system. Pressures and partial pressures in the reactor chamber were measured with a thermocouple gauge and by flows through calibrated leaks. Total pressures were between 0.1 and 1.0 Torr. This range was chosen because it is sufficiently low that the surface reactions are kinetically controlled and the gas composition and temperature in the reactor chamber are uniform. The diffusion time across the 250 ml spherical chamber is ≤ 0.1 sec while the residence time was ≥ 1 sec. A gas molecule therefore makes many more collisions with cold walls than with the heated filament. Under these conditions (*11*) the system may be approximated as a well-mixed reactor with the gas at room temperature,

$$r_i = \frac{q\Delta P_i}{ART_g}, \qquad (5)$$

where r_i is the rate of production of species i per unit catalyst area A and q is the volumetric flow rate. Reaction rates are thus simply obtained by measuring initial and final partial pressures, surface area, and system volume and pumping speed. The above equation assumes that the mixed reactor equation is applicable. A more stringent requirement is that the gas composition at the surface be the same as that in the entire chamber. Calculations indicate (*11*) that this should be valid for $P = 0.1$ Torr, but possibly not for pressures greater than 1 Torr.

Surface temperatures were maintained by resistive heating and were measured by a four lead potential network from the known resistivity versus temperature of the three wires. Short lengths of 0.003 in diameter Pt were welded between the current leads and the wires to obtain uniform temperatures. For high temperatures where an optical pyrometer could be used, temperatures were observed to vary by no more than 100°C over the length of the wires and these deviations occurred only over short segments near the ends.

Gas compositions were determined by leaking a small fraction of the gases in the reaction vessel through a pinhole in Al foil into a differentially pumped quadrupole mass spectrometer, and signals were displayed on an electrometer or strip chart recorder. Sensitivities for various gases at operating conditions were calibrated with known gas mixtures. All species concentrations could be measured readily except for NH_3 and H_2O which adsorbed on the walls of the mass spectrometer chamber and exhibited time dependent signals. Compositions were determined mainly from the N_2, NO, and O_2 signals, although overall stoichiometric balances were checked occasionally. Data were generally reproducible to within ±10% over long periods and for different wires of the same material.

For most experiments all three wires were mounted in the same reactor in order to compare relative rates on the three metals. Wires which had been used many hours under all conditions of temperature and composition were examined by scanning electron microscopy. Pt and Rh were quite smooth and exhibited only grain boundaries spaced ~0.05 cm apart. However extensive etching occurred on Pd which formed a structure permeated with small pits ~2 μm in diameter. Therefore, while surface areas of Pt and Rh were close to the geometrical areas, comparison of reaction rates on Pd with those on Pt and Rh may be inaccurate. However, it is possible that reaction occurs mostly on external surfaces, and rates will be reported on that basis. Examination of wires and ribbons of Pt which had been heated in O_2 and in NH_3/O_2 mixtures by Auger electron spectroscopy (AES) and sputtering techniques showed that the surfaces were generally free of contaminants and contained only monolayers of oxygen or carbon (*12*). Most of the results reported here were obtained at a total pressure of 0.115 Torr. Data were generally consistent with results reported previously (*1*) at pressures of approximately 1 Torr, although present results are considered more reliable.

We shall fit our rate expressions using LH type expressions (*7*), i.e., for a unimolecular surface reaction $A \rightarrow B$,

$$r = k_R\theta_A = \frac{k_R K_A P_A}{1 + K_A P_A}, \tag{6}$$

and for a second order surface reaction A + B → products,

$$r = k_R\theta_A\theta_B = \frac{k_R K_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B)^2} \tag{7}$$

or

$$r = k_R\theta_A\theta_B = \frac{k_R K_A K_B P_A P_B}{(1 + K_A P_A)(1 + K_B P_B)}. \tag{8}$$

These are the standard forms usually assumed for these reactions with competitive [Eq. (7)] or noncompetitive adsorption [Eq. (8)]. These equations would be strictly valid only for Langmuir isotherms ($s \sim 1 - \theta$) and for a homogeneous surface. Further, all of the k's should in general be functions of coverage and therefore of pressure.

However, we shall show that our rate expressions can be fit fairly well with expressions of this form with all parameters assumed to be *functions of temperature alone*. The parameters certainly contain coverage and crystal plane dependences, but we suggest that these may be effectively lumped into constants which are functions only of temperature.

Such fits should only be given significance if they reproduce data over a wide range of composition and temperature. The present results are obtained between 10 and 90% of each reactant and between 200 and 1400°C. The major emphasis in this work will be on the temperature dependences predicted by these equations. If the reaction rate constant is of the form,

$$k_R = k_{0R} \exp(-E_R/RT), \qquad (9)$$

and the adsorption constant is of the form,

$$K_A = K_{0A} \exp(E_A/RT), \qquad (10)$$

then it is easy to show (*11*) that Eqs. (6)–(8) predict rate maxima with temperature if the heats of adsorption E_A and E_B are sufficiently large.

We fit our experimental rates to expressions similar to Eqs. (6)–(10) with a nonlinear least squares program which used a Gauss–Newton procedure to search for optimum choices of parameters to fit data. Points were weighted equally, and no curves or particular points were excluded from the fitting program. Our parameters are those obtained directly by least squares fits to data; they are not adjusted to agree with expected magnitudes or even signs of any parameters. There are multiple extrema in a nonlinear fit of this type, but for fits of a single reaction the "best" fits were always independent of initial values used in search routines.

We emphasize that the preexponential factors and activation energies obtained by such a procedure should not be expected to be interpretable quantitatively in terms of actual reaction or adsorption parameters. However, the lumped parameters should be roughly representative of these quantities and should permit one to assess the validity of various rate expressions and to compare behavior on different metals.

RESULTS AND DISCUSSION

Individual Reaction Rates

Decomposition of NH_3 and NO. Figure 1 shows the rate of N_2 production on Pt, Rh, and Pd from NH_3 at a pressure of 0.115 Torr. The rates do not appear to go through maxima as was previously reported for Pt at higher pressures. It is possible that the rates would attain maxima at higher temperatures or that $E_R > E_{NH_3}$, in which case no maximum would be predicted.

NO decomposition is even slower than NH_3 decomposition, and it was difficult to obtain accurate rate measurements with the residence times of our experiments. On Pt and Pd at an NO pressure of 1.0 Torr the rate of N_2 formation was $\sim 1 \times 10^{-8}$ moles cm^{-2} sec^{-1} for temperatures between 1200 and 1500°C. This is over 100 times slower than either bimolecular reaction involving NH_3.

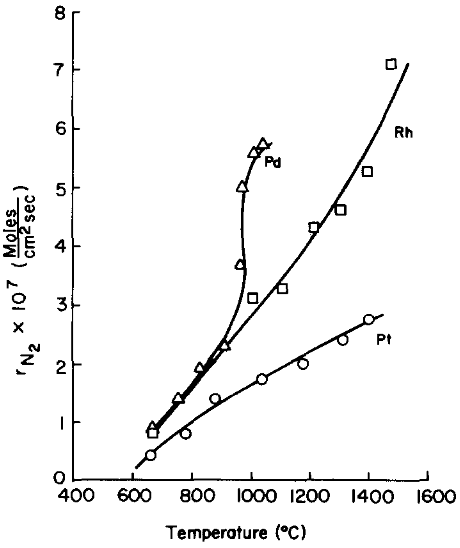

FIGURE 1.

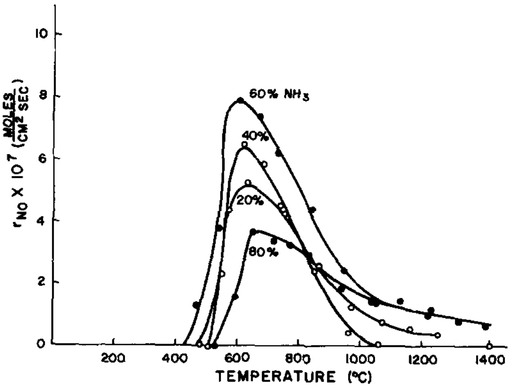

FIGURE 2.

On Rh the rate was as high as 1×10^{-7} moles cm^{-2} sec^{-1} at 0.115 Torr, but the rate did not go through a maximum up to 1600°C. Rates of NO decomposition on Rh could be fit by the expression

$$r_{N_2}\ (\text{moles/cm}^2\ \text{sec Torr}) = 2.2 \times 10^{-3}\, P_{NO} \exp\left(-\frac{26{,}000}{RT}\right).$$

The higher rate of this reaction is probably due to the stronger adsorption of NO on Rh. As considered below, similar behavior is also observed in bimolecular reactions involving NO.

Reaction between NH_3 and NO. Figures 2, 4 and 6 show measured rates of NO consumption versus temperature on Pt, Rh, and Pd, respectively. Data were obtained with a constant total pressure of 0.115 Torr, and NH_3 initial compositions are indicated in Figs. 2, 4 and 6.

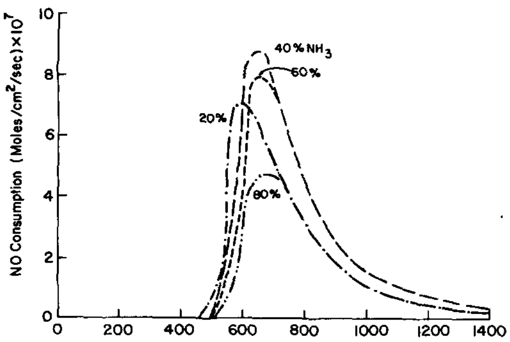

FIGURE 3.

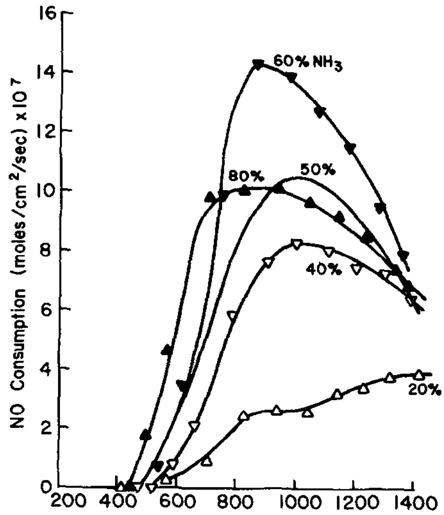

FIGURE 4.

These data were fit assuming competitive adsorption of NO and NH_3, Eq. (7). Calculated rates at these compositions are shown in Figs. 3, 5 and 7, and corresponding rate parameters are given in Table 1. For Pt and Pd peak temperatures are lower for low NH_3 concentrations, indicating that NH_3 adsorption was stronger than NO adsorption. Therefore fits for these metals were made assuming K_{NO} to

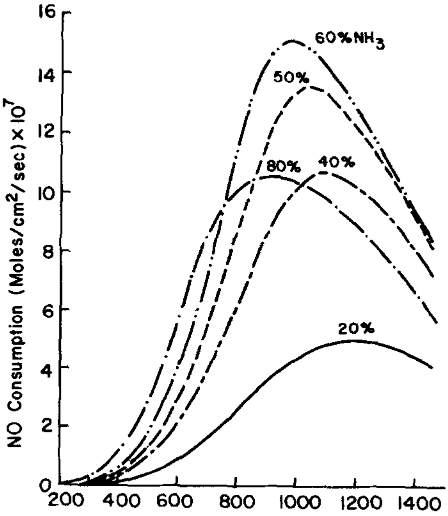

FIGURE 5.

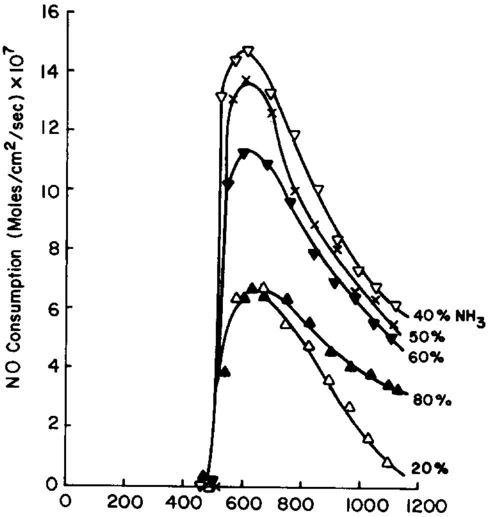

FIGURE 6.

be zero (a four parameter fit). In contrast to Pt and Pd, the peak temperatures on Rh are higher for low NH_3 concentrations, indicating that NO is more strongly adsorbed than NH_3. A six parameter fit including K_{NO} and K_{NH_3} was found to give best agreement with the broader rate curves on Rh. The major discrepancies between experimental and calculated curves on all metals occur at low NH_3 concentrations; otherwise there are no systematic differences.

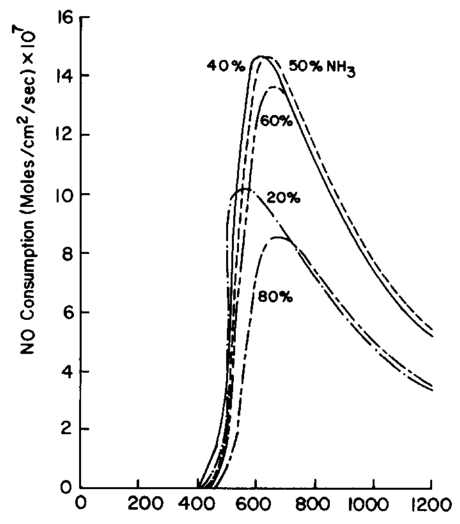

FIGURE 7.

TABLE 1

RATE PARAMETERS FOR NO + NH_3 REACTION[a]

Metal	k_{0R}	E_R (kcal/mole)	k_{0NH_3}	E_{NH_3} (kcal/mole)	k_{0NO}	E_{NO}
Pt	5.3×10^2	28	1.3×10^{-10}	45	—	—
Rh	2.8×10^2	9.5	2.4×10^{-2}	34	—	—
Pd	3.2×10^{-4}	15.3	2.8×10^{-10}	17.7	2.6×10^{-2}	20.7

[a] Calculated by fitting rate data of Figs. 2, 4, and 6 to Eqs. (7), (9), and (10). Preexponential factors in units of moles/cm² sec Torr.

Ammonia Oxidation Kinetics

Figures, 8, 9, and 10 show rates of NO and N_2 formation versus temperature on Pt, Rh, and Pd, respectively. The total pressure in the NH_3/O_2 feed was 0.115 Torr in all experiments, and the initial percentages of NH_3 are indicated in Figs. 8–10. These curves are generally similar to those reported previously on Pt at a total pressure of 0.75 Torr, except for some additional structure in the previous curves. We now know that the apparently complex behavior of some of the previous curves was caused by inaccurate measurement of NO and N_2 concentrations in the mass spectrometer.

The only region in which the accuracy of measurements was poor was between 200 and 400°C. Here, as in the NO + NH_3 reaction, the onset of N_2 production was frequently too abrupt to follow closely and, while results appeared to be identical for increasing and decreasing temperatures, it was not possible to fill in complete curves. Data in this region are therefore shown as essentially discontinuous rises in most cases. There are several possible causes for such behavior. First, it is possible to have multiple steady states in an isothermal well-mixed reactor with Langmuir–Hinshelwood kinetics (*13*). This would lead to truly discontinuous changes in steady state rates with temperature,

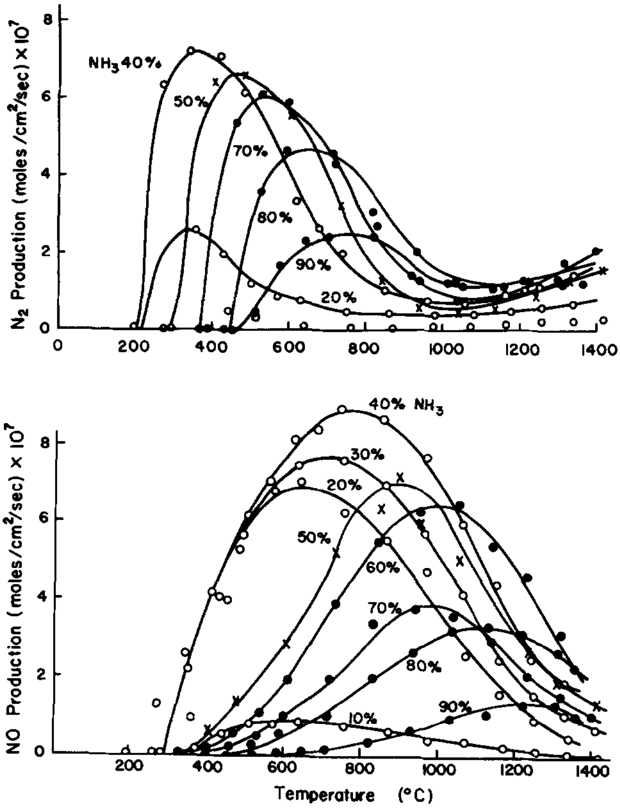

Figure 8.

although we caclulate that steady states are probably unique for our kinetics and residence times. A second possibility is multiple states caused by heat generated by the reaction. In most of these experiments we did not use an automatic temperature controller, and wire temperatures were difficult to control precisely in this region because of reaction heating. A third possibility is that contaminants may be on the surface at low temperatures which desorb or are oxidized at these temperatures. The reversibility and reproducibility of our data argue against these effects, but they cannot be completely excluded from present results.

We next attempt to fit the results of Figs. 8–11 to LH rate expressions. We note first that this is a very complex system of reactions. At least four kinetically independent reactions are involved, Eqs. (1)–(4), even if one ignores product species other than NO and N_2. Also, because in a sequence of reactions a product species may continue to react without desorption and readsorption, surface concentrations and partial pressures may not be related through adsorption isotherms for such species. Nevertheless, we shall attempt to see whether simple reaction rate expressions are useful in analyzing the rather complex behavior apparent in Figs. 8–11 and also to obtain working expressions for prediction of reaction selectivities at high pressures.

A qualitative examination of the oxidation rates and the individual unimolecular and bimolecular reaction rates shows that the series-parallel processes [Eqs. (1)–(4)] seem to describe the NH_3 oxidation process fairly well. Figure 12 shows rates of NO and N_2 production in NH_3 oxida-

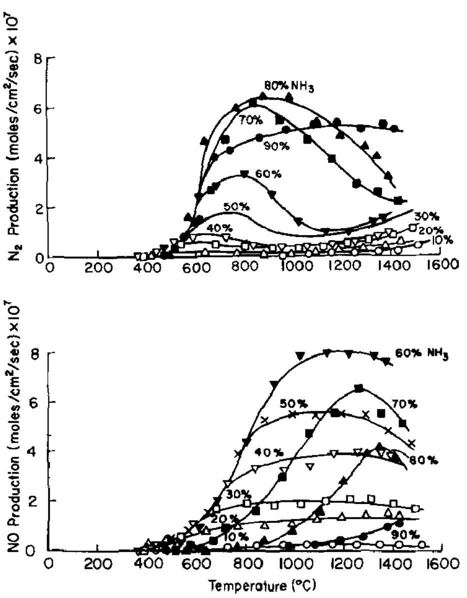

FIGURE 9.

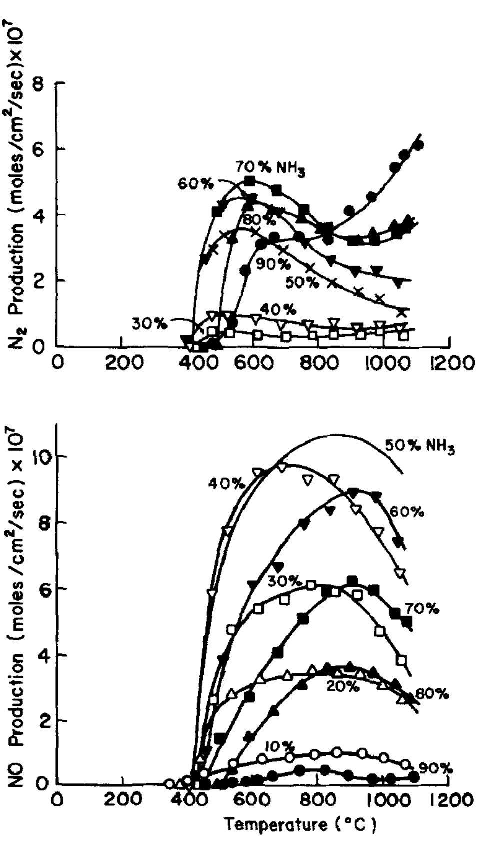

FIGURE 10.

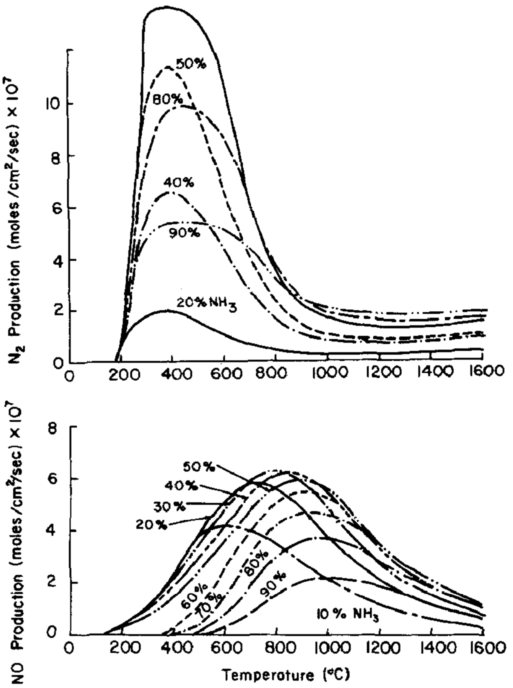

FIGURE 11.

tion (solid curves) and in the individual reactions (broken lines). The curves shown here are from experimental data at a total pressure of 0.115 Torr and for reactant compositions of 50% NH_3 in $NO + NH_3$ and $O_2 + NH_3$ mixtures. The individual reaction rates are measured at different compositions than those in the oxidation reactions and therefore comparisons should be expected to have only qualitative significance. For example, all single reactions were measured in the complete absence of O_2, and consequently influences of adsorbed oxygen on reaction rates would not be apparent in these measurements. In spite of these differences, the production of N_2 in NH_3 oxidation is clearly indicated as arising mostly from the $NO + NH_3$ reaction at low temperatures ($T < 1000°K$) and from the decomposition of NH_3 at high temperatures ($T > 1200°K$). Unimolecular decomposition of NO appears to be quite unimportant except on Rh at high temperatures.

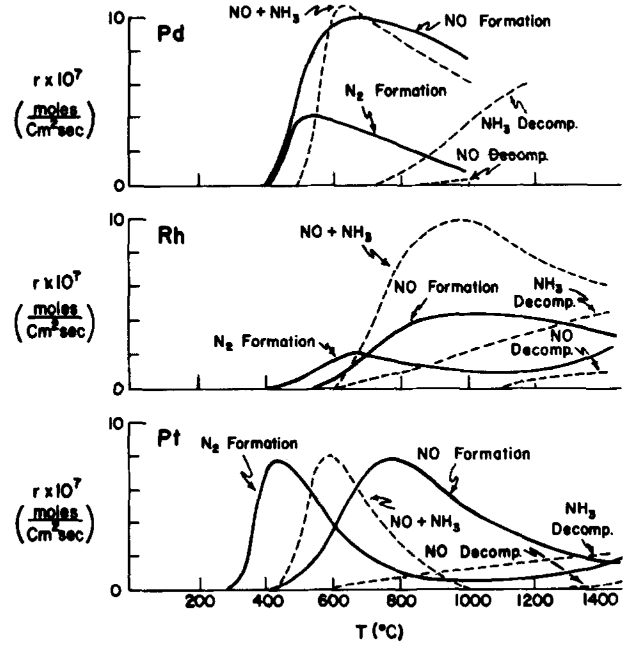

FIGURE 12.

Several more qualitative features of the oxidation kinetics are evident from the general behavior at different compositions. The onset of N_2 production occurs at lower temperature at lower NH_3 compositions. The rate is therefore of *negative order* with respect to NH_3 in this region, and this suggests *competitive* adsorption of NH_3 and some species, in agreement with the kinetics previously shown to fit the $NO + NH_3$ reaction [Eq. (7)]. On the other hand the NO production rate from NH_3 and O_2 (Figs. 8–10) is independent of the NH_3 composition in excess O_2 at low temperature. Zeroth order kinetics at low temperatures suggest *noncompetitive* adsorption of NH_3 and oxygen [Eq. (8)]. Further, one expects that oxygen should adsorb dissociatively to react, and therefore its isotherm should be of the form

$$\theta_0 = K_{O_2}^{1/2} P_{O_2}^{1/2} / (1 + K_{O_2}^{1/2} P_{O_2}^{1/2}). \quad (11)$$

From these simple arguments one would expect that the rates of NO and N_2 production might be represented by expressions of the form

$$r_{NO} = \frac{k_1 P_{NH_3} P_{O_2}^{1/2}}{(1 + K_{NH_3} P_{NH_3})(1 + K_{O_2}^{1/2} P_{O_2}^{1/2})} \quad (12)$$

and

$$r_{N_2} = \frac{k_2 P_{NH_3} P_{NO}}{(1 + K_4 P_{O_2} + K'_{NH_3} P_{NH_3})^2} + \frac{k_3 P_{NH_3}}{1 + K_4 P_{O_2} + K'_{NH_3} P_{NH_3}}. \quad (13)$$

The term $K_4 P_{O_2}$ has been added in the unimolecular and bimolecular reactions of NH_3 which were not present in previmus fits of the reactions individually because now the reactions occur in a high partial pressure of O_2. These are obviously lumped parameter equations. It was not possible to fit the more rigorous equations to the experimental data because of instabilities resulting from the larger number of adjustable parameters. The 14 parameters in Eqs. (12) and (13) should contain the essential features of the rate process as sketched above.

Figure 12 shows calculated rates of NO and N_2 formation versus temperature on Pt using Eqs. (12) and (13) to fit the data of Fig. 8. The rate parameters in Eqs. (12) and (13) were

$$r_{NO} = \frac{3.4 \times 10^{-8} \exp(+21{,}700/RT) P_{NH_3} P_{O_2}^{1/2}}{[1 + 8 \times 10^{-2} \exp(+4400/RT) P_{O_2}^{1/2}][1 + 1.6 \times 10^{-3} \exp(+25{,}500/RT) P_{NH_3}]} \tag{14}$$

and

$$r_{N_2} = \frac{4.2 \times 10^{-9} \exp(+26{,}000/RT) P_{NO} P_{NH_3}}{[1 + 5.4 \times 10^{-2} \exp(10{,}900/RT) P_{O_2} + 4.5 \times 10^{-6} \exp(20{,}900/RT/P_{NH_3}]^2} + \frac{2.2 \times 10^{-6} \exp(-570/RT) P_{NH_3}}{1 + 5.4 \times 10^{-2} \exp(+10{,}900/RT) P_{O_2} + 4.5 \times 10^{-6} \exp(20{,}900/RT) P_{NH_3}}, \tag{15}$$

with pressures in Torr and rates in units of moles cm^{-2} sec^{-1}.

In formulating reaction rates in terms of Langmuir–Hinshelwood kinetics one assumes implicitly that adsorption and desorption steps are much more rapid than reaction so that coverages and pressures may be related by an adsorption isotherm. Our reaction rates were always less than 10^{-2} of the reactant fluxes to the surface, and we have used model calculations to show that LH expressions should be fairly accurate even when adsorption and desorption rates are comparable to reaction rates.

However, in the case of N_2 formation from NO, a reaction intermediate, this approximation may be invalid because it is not necessary that NO first evaporate and then readsorb to react with NH_3. We fit the experimental rate data on Pt to a model which included this possibility by solving the appropriate gas and adsorption mass balance equations simultaneously (*11*). The least squares program invariably set the parameters for NO evaporation and adsorption equal to their lower bounds. However, this model gave fits to the experimental data which were inferior to those using Eqs. (12) and (13).

Comparisons Between Metals

In this section we discuss qualitatively the differences in various reaction rates in terms of adsorption parameters on the three metals. Rates cannot be described simply as being lower or higher on a particular metal but must be described through the dependences on *temperature*. Figure 12 shows that, while all reactions have comparable rates at their maxima, these occur at temperatures which differ by several hundred degrees. The rates and selectivity to be expected at a particular catalyst temperature and gas composition are therefore dominated by the temperature dependences of various rates. The dependences on partial pressure are also strongly influenced by the shifts in rate maxima with temperature.

The differences between the individual bimolecular reactions appear to be caused mainly by the stronger bonding of NO on Rh compared to Pt and Pd. This produces a higher rate of NO decomposition on Rh and causes the bimolecular reaction to be shifted to higher temperature. At low temperatures ($T < 700°C$) Rh is a very poor catalyst for the NO + NH_3 reaction while at high temperatures ($T > 900°C$) Pt is a poor catalyst but Rh is a good one. The strength of NO adsorption compared to NH_3 (Figs. 2, 4 and 6) results in quite different reaction rate pressure dependences for these gases on the three metals, and these pressure dependences shift completely within a few hundred degrees as the rates pass through their maxima. This difference can be seen from the "heats of adsorption," the E_{NH_3} and E_{NO} quantities in Table 1, but, while these are frequently similar to reported literature values of heats of adsorption, we do not regard either our values or literature values to be sufficiently accurate to justify detailed comparisons. The preexponential factors in the adsorption constants K_{0j} are ratios of sticking coefficients to desorption preexponential factors ν_{0j},

$$K_{0j} = \frac{s_{0j}}{\nu_{0j}(2\pi mkT)^{1/2}}, \qquad (16)$$

and, if the initial sticking were unity and ν_0 were 10^{13} sec^{-1}, then the "normal" value of K_{0j} would be $\sim 10^{-7}$ Torr^{-1}. Some of the adsorption constants in Table 1 are close to this value, but the results and the fits do not have sufficient accuracy to permit one to associate deviations with low s_0 or with anomalous preexponential factors.

The interpretation of the oxidation rates is even more difficult because of the number of independent reactions. However it seems clear that the maximum in N_2 production is associated with the $NH_3 + NO$ reaction at low temperatures and with NH_3 decomposition (along with NO decomposition on Rh) at high temperatures. The selectivity of oxidation to NO is thus determined by the temperatures at which the three rates are high. On all metals there is a temperature "window" between 700 and 1000°C where the selectivity to NO is high, but the maximum selectivity is larger for Pt (94% conversion to NO) than for Pd (90% conversion to NO) or Rh (79% conversion to NO). The highest selectivity on Pd occurs at the highest temperatures where metal evaporation is significant, so that at these pressures Pt is by far the best catalyst for NO production. The reason that a high selectivity is not observed on Rh is because the $NO + NH_3$ reaction maximum almost overlaps that for NH_3 oxidation, again presumably because of strong adsorption of NO on Rh.

Prediction of High Pressure Selectivity

In the high pressure production of NO from NH_3 and air over Pt–10% Rh gauzes (*2–4*) the maximum selectivity of 95–99% is attained with ~10% NH_3 in air and gauze temperatures of ~900°C. This is observed in industrial operation at 1–8 as well as in our laboratory studies in NH_3/air mixtures at 1 atm (*1*). Under these conditions the reactions are mass transfer controlled in the sense that NH_3 consumption can be calculated from mass transfer coefficients to the surface of the Pt gauzes (*14*). However, since selectivity is the important parameter, the relative rates of production of NO and N_2 are still governed by the kinetics of the individual reactions even though essentially all NH_3 is consumed. In this section we shall attempt to use the rate parameters obtained in the 0.1 Torr reaction to calculate the selectivities at high pressure as functions of composition, gauze temperature, and contact time.

A simple model of the gauze catalyst is that of an isothermal stirred tank reactor with a mass transfer coefficient calculated from the flow characteristics over the gauze,

$$r_i = F[(P_i^g - P_i^s], \qquad (17)$$

with P_i^g the pressure of the limiting reactant far from the surface and P_i^s the pressure near the surface. A typical industrial throughput at 1 atm of 10% NH_3 in air is 100 lb NH_3 day^{-1} oz catalyst^{-1} with catalyst an 80 mesh gauze of 0.003 in. diameter wire. From this information we estimated a mass transfer coefficient $F = 5.8 \times 10^{-8}$ moles cm^{-2} sec^{-1} Torr^{-1}. This is smaller than the value obtained from the smooth wire area by a factor of ~10, which is reasonable because of surface roughness in the industrial gauze.

Conversions were calculated by solving Eqs. (14), (15) and (17) simultaneously by eliminating P_i^s between then. Figure 13 shows the calculated selectivity of conversion of NH_3 to NO on Pt versus temperature using the stirred tank model and the kinetic parameters of Eqs. (14) and (15).

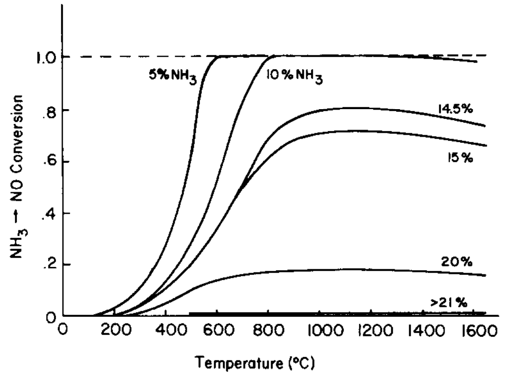

FIGURE 13.

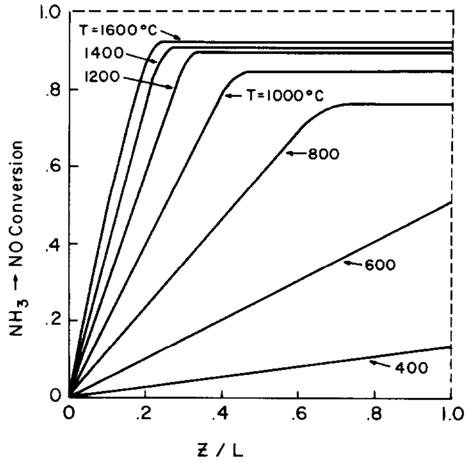

FIGURE 14.

This reproduces fairly well the observed high selectivity up to 10% NH_3 and the rapid falloff with feed composition as one approaches the stoichiometric ratios (14.1% for conversion to NO and 21% to N_2). The maximum selectivity at 10% NH_3 is obtained at ~900°C, exactly that observed to be optimum in the industrial reactor. It should be noted, however, that the selectivity is not a sensitive test of choices of all rate parameters because these merely determine the rate limiting concentrations versus temperature. At high temperatures ($T > 1000°C$) the selectivity is observed to fall rather rapidly, while a fairly gradual decrease is calculated from this model. This is probably caused by homogeneous boundary layer reactions in the reactor which consume NH_3 and produce N_2. There have been a number of reports of heterogeneously induced chain reactions in the gas phase for this reaction at high temperatures (*15*).

To test the sensitivity of the calculated selectivity on the reactor model, we also made calculations assuming 10 stirred tank reactors in series, each with a reactor parameter F ten times that assumed previously. Figure 14 shows the calculated conversion to NO versus position in the gauze z/L for several gauze temperatures. It is interesting that this model gives lower yields of NO than does the corresponding single stirred tank reactor because the initial product NO can react with unreacted NH_3 further down the gauze. This explains the contact time effect, known since Andrussow's early experiments, in which the NO yield decreases with increasing contact time. The profiles shown in Fig. 14 are in agreement with the estimates that in industrial reactors the reaction occurs mainly in the first one-half of the bed length (*2*).

SUMMARY

The reaction mechanism of the catalytic oxidation of ammonia on platinum has been the object of an enormous number of experimental studies over the past 50 yr, yet it remains uncertain. We feel that the most useful kinetic model of the reaction is one that avoids detailed "atomistics" and describes the overall reaction in terms of the relatively simple series-parallel mechanism, Eqs. (1)–(4). The three individual surface reaction steps may then be modeled by one of the various, classical Langmuir–Hinshelwood kinetic forms. Our objective in this study was to obtain, compare, and analyze steady state rate data at low pressure for all of the individual reaction steps in the same reactor geometry, on

the same catalyst surface, and over the widest possible temperature range (200–1500°C). This last was most important for demonstrating the LH character of the kinetics. Finally, as regards activity and selectivity, platinum was compared with palladium and rhodium, two metals often used in similar reactions.

The NO/N_2 selectivity in the oxidation reaction on Pt may be described qualitatively as follows. The surface reaction forming NO from NH_3 and O_2 is extremely rapid and proceeds measurably even below 200°C. In the low temperature regime, though, the NO formed may be bound rather strongly to the surface and may readily react with NH_3 to form N_2. With increasing temperature more of the NO formed escapes the surface and the selectivity begins to shift toward net NO production. This is a key feature of LH kinetics – decreasing surface reaction rate due to rapidly decreasing surface coverage of reactant.

At some temperature ($\gtrsim$ 800(C) virtually all of the NO formed escapes (in O_2 excess conditions), but the peak NO rates shift to higher temperatures with increasing NH_3 pressure as NH_3 hinders the escape. It also appears that the NH_3–O_2 reaction to NO itself becomes adsorption limited at high temperatures and the overall reaction then degrades to NH_3 decomposition, the selectivity shifting back to N_2.

Palladium and rhodium were found to have roughly the same peak activity as platinum, although the effective palladium surface area may have been increased by several times over its geometric area and the temperature regime of activity for rhodium was much higher than that for the other two meals. A distinctive characteristic of the NO/N_2 selectivity on Pt is the relatively wide separation in temperature of the N_2 and NO peaks while there is much more overlap for Pd and Rh. For Pd especially it appears that the NO- and N_2-forming reactions peak together, decreasing the maximum attainable NO/N_2 selectivity. It should be noted, though, that in O_2 excess the low temperature NO–NH_3 reaction is suppressed to a much greater extent on Pd and Rh than on Pt.

Most of the individual reaction rate data was subjected to analysis in Langmuir–Hinshelwood terms – the unimolecular LH form for NH_3 decomposition on Pt and the LH form of competitive bimolecular reaction in the NO–NH_3 reaction on all three metals. The kinetic constants of Table 1 should not, however, be taken literally as the adsorption or reaction parameters that the model implies because all the data fits are at best only semiquantitative. Also, we find certain of the fitted constants changing from one reaction to another when they should correspond, in theory, to the same adsorption parameter. That is, the addition of NO to the system appears to alter the adsorption characteristics of NH_3 as determined in the NH_3 decomposition reaction, and the addition of O_2 in the overall oxidation reaction alters them even more. The change here is noticeable in the qualitative nature of the data. On Pt and Pd the low temperature NO–NH_3 reaction proceeds at lower temperatures when oxygen is present, the temperature of incipient reaction shifting continuously from 200 to 500°C (the latter the same as in the pure NO–NH_3 reaction) with decreasing O_2 concentration.

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