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Kinetics of NH_3 Decomposition on Iron at High Temperatures[1]

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The kinetics of NH_3 decomposition on polycrystalline iron wires between 600 and 1250 K and pressures between 0.05 and 1 Torr are measured and correlated with examination by SEM and AES. Reproducible rates are obtained in pure NH_3 which can be fit accurately at all temperatures and pressures by a Langmuir–Hinshelwood (LH) unimolecular rate expression with reaction and desorption activation energies of 49,600 and 39,600 cal/mole, respectively.

Hydrogen alters the decomposition rate to a higher value which for high hydrogen pressures is independent of P_{H_2} and can also be fit by a LH expression. Results are interpreted in terms of surface nitride in pure NH_3 and nitride-free iron in hydrogen.

Reaction in NH_3 produces much more rapid and extensive facetting than does heating in vacuum, and repeated cycling through the α–γ phase transition in NH_3 produces even more extensive facetting of the surface. This is apparently caused by preferential attack of NH_3 at dislocations induced at the surface by the phase transformation. No discontinuity in rate was observed in crossing the transition temperature.

INTRODUCTION

This paper is the fifth in a series designed to examine kinetics of simple reactions on metal surfaces over a wide range of temperature, pressure, and gas composition in order to obtain accurate rates of catalytic reactions. We have shown that rates of NH_3 decomposition (*1*), $NH_3 + NO$ (*2*), $CO + O_2$ (*3*), and NH_3 oxidation (*2, 4*) on Pt, Rh, and Pd can be fit quite well by simple Langmuir–Hinshelwood (LH) rate expressions and that temperature-dependent reaction rate constants and adsorption constants can be extracted from analysis of these results. For NH_3 decomposition on Pt (*1*) we have shown that a LH expression gives quantitative agreement with all data in NH_3 and H_2 mixtures, and we have recently obtained analogous results on four single crystal planes of Pt (*5*).

Iron is a much studied catalyst for NH_3 decomposition because of interest in the synthesis reaction (*6*). Experiments have generally been carried out over limited temperature ranges with high hydrogen pressures, and most experiments have employed Fe in singly, doubly, or triply promoted forms. No completely consistent rate expression exists (not particularly surprising in view of the variations in conditions and forms of the catalyst), although data have usually been correlated (*6*) with the Temkin–Pyzhev (*7*) rate expression

$$r = k\left(\frac{P_{NH_3}}{P_{H_2}^{\frac{3}{2}}}\right)^{\alpha}, \tag{1}$$

with α a semiempirical constant obtained by assuming the heat of adsorption of NH_3 to be a linear function of NH_3 coverage. Other rate expressions have also been suggested to explain experimental results (*8–10*).

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An interesting property of Fe for this reaction is its ability to form nitrides in NH_3 at low hydrogen pressures according to the reaction

$$2x\ \mathrm{Fe} + 2\ \mathrm{NH_3} \rightleftarrows 2\ \mathrm{Fe_xN} + 3\ \mathrm{H_2}, \quad (2)$$

although most experiments have been carried out at hydrogen pressures sufficiently high that no bulk nitrides are stable. The structures of Fe catalysts in decomposition and synthesis have been extensively characterized by surface area, X-ray diffraction, and Mössbauer spectroscopy (*11, 12*), but mostly on high area supported and promoted surfaces. The kinetics and equilibrium properties of nitridization in NH_3 have also been studied (*13–16*).

Our interest here is to obtain rates on pure iron over a wide range of temperature and to examine the influence of nitrides on kinetics and surface morphology. Our temperature range is higher than that used for the synthesis reaction, although we examine a wide range of adsorbate coverages as inferred by changing orders of the reactions.

EXPERIMENTAL

Rates were measured in a greaseless glass and metal flow system as described previously (*1, 2*) with inlet and outlet flow lines trapped with dry ice–acetone baths. Gas composition was monitored by a differentially pumped quadrupole mass spectrometer, and rates were obtained from partial pressures using the well-mixed reactor equation. Conversions were always less than 10% so that rates were those essentially at the inlet composition. From calibrations of flow rates, pressures, and mass spectrometer sensitivity, rates obtainable in this system are believed to be accurate to ±10%, although for Fe changes in surface area described below resulted in a reproducibility less than for Pt.

Surfaces were 0.25-mm-diameter polycrystalline Fe wires of 99.998% purity which were heated resistively. Temperatures were measured from the wire resistance using a four-lead network and from Pt–Rh thermocouples spot welded to the wires. The latter eliminated spurious results caused by bulk nitride formation or morphology changes.

Because rates are measured from the partial pressure of nitrogen, it is essential that a negligible fraction of nitrogen produced by NH_3 decomposition dissolves in the iron. Appreciable nitrogen uptake would also alter the wire resistance by which the temperature was controlled. In a series of experiments using resistivity and thermocouple measurements it was ascertained that the wires changed in resistivity by less than 1% which represents less than 1 atom percent nitrogen (*13*). Further, the resistivity versus temperature curve duplicated closely that published for Fe (including the break at the Curie temperature) and the wire moved noticeably when crossing the α–γ phase transition temperature (nitrogen sharply reduces this temperature). This behavior was identical for untreated wires as well as for wires heated in ~1 Torr of NH_3 at 1200 K for several hours, except after repeated cycling in NH_3, as will be discussed later.

Although dissolved nitrogen and nitrides should, by equilibrium in Eq. 2, be stable in NH_3 except at higher H_2 pressures than we have employed, it is well known (*16*) that nitrides are very difficult to form by exposure to NH_3 above ~1000 K because nitride decomposition to form N_2

$$2\ \mathrm{Fe_xN} \rightleftarrows 2x\ \mathrm{Fe} + \mathrm{N_2}$$

becomes significant at high temperatures and yields an equilibrium N_2 dissociation pressure of many atmospheres.

We searched without success for transients in N_2 production upon step heating or cooling of the wires in NH_3 between 900 and 1200 K. These may be significant if the solubility of nitrides were exceeded or if decomposition to form N_2 became important upon changing the temperature. We estimated that bulk concentrations much less than 1% should be observable but not nitrogen confined to a few monolayers near the surface. The diffusion coefficient of nitrogen dissolved in Fe is such that equilibrium throughout the wire should be attained in a few seconds above 1000 K (*17*). We conclude from these observations that the bulk of the Fe wires were α or γ phases essentially free of dissolved nitrogen or nitrides under all conditions except possibly following repeated cycling from room temperature.

The reactor was pumped by a trapped mechanical pump which gave a background pressure of $\sim 10^{-3}$ Torr. This is obviously inadequate to prevent carbon and oxygen contamination, but wires were heated only in flowing NH_3 or $NH_3 + H_2$ mixtures at pressures considerably higher than this.

Using Auger electron spectroscopy (AES), we measured composition versus depth profiles on two iron samples which had been used in the reactor. Iron foils of the above purity were etched in HCl and sealed into the reactor. After heating in NH_3 the foils were removed and kept under vacuum until insertion into an ultrahigh vacuum AES-sputtering system.

The AES peak heights of Fe, O, C, N, and Cl versus depth from surface of a foil which had never been heated and from a foil heated at 1200 K in NH_3 at 0.5 Torr for 2 hr was obtained. Both exhibited surface oxides as expected from their exposure to air before insertion in the AES system, but on the surface heated in NH_3 the oxide was only ~20-Å thick (estimated by the sputtering rate of Fe), while on the unheated wire the oxide layer was ~500-Å thick. Chlorine was present at the surface of the unheated wire from the etching treatment but there were no other elements detectable by AES except for N near the surface of the foil heated in NH_3. We conclude from these measurements that our Fe surfaces are essentially free of oxide (in the reducing atmosphere of the reactor), carbide, or other contaminants at concentrations above the detectability of AES. The absence of oxides and carbides is also predicted thermodynamically in the presence of reducing gases such as NH_3 and H_2 (*16*).

All wires were examined by SEM after removal from the reactor. One set of wires was heated to 1250 K on the microscope stage at a pressure of 5×10^{-7} Torr to observe the effect of heating and temperature cycling on surface morphology.

Kinetics in Pure NH_3

Figure 1 shows the measured rate of NH_3 decomposition r_R versus temperature in

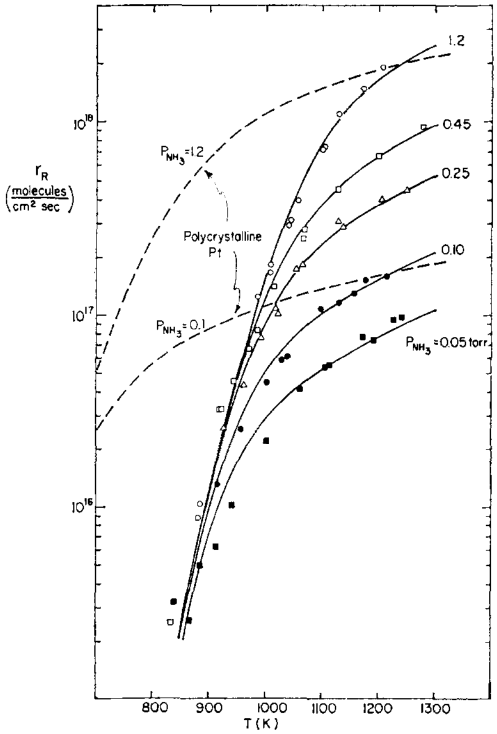

FIG. 1. Rate of NH_3 decomposition r_R on polycrystalline iron versus surface temperature in pure NH_3 at pressures indicated. Solid curves are calculated assuming a Langmuir–Hinshelwood rate expression, Eq. 3, with temperature-dependent parameters from Eqs. 6 and 7. Dashed curves are rates on polycrystalline platinum from ref. *1*.

pure NH_3 between 0.050 and 1.2 Torr. The system was capable of measuring rates down to $\sim 10^{15}$ molecules cm^{-2} sec^{-1} (a reaction probability of 10^{-6} at 1 Torr), and this sensitivity limited the minimum temperature to $\sim$850 K for Fe. The maximum temperature was limited by Fe evaporation above 1250 K.

Data shown were obtained on two wires, and all data on approximately 10 wires were consistent with Fig. 1 after heating for a few minutes in NH_3, except for situations where SEM showed that the wire area had increased. Immediately after insertion of a fresh wire into the reactor, the rates were lower by a factor of about 10, but within 15 min of heating in NH_3 at $T \sim 1200$ K the rate was always within 30% of data shown. We attribute the initial increase to the reduction of oxide and carbide contaminants on fresh wires.

Figure 2 shows a plot of r_R versus P_{NH_3} for different temperatures for data of Fig. 1. At 1200 K, the rate is proportional to $P^{0.98\pm0.05}$ except for the highest pressure.

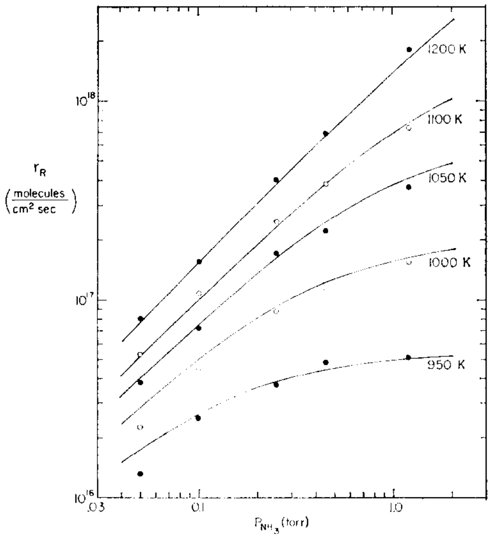

FIG. 2. Rate of NH_3 decomposition versus P_{NH_3} from data of Fig. 1 at temperatures indicated. At high temperature the rate is first order in P_{NH_3}, but at low temperatures the rate approaches zero order at high pressures. The solid curves are calculated from Eqs. 3, 6, and 7.

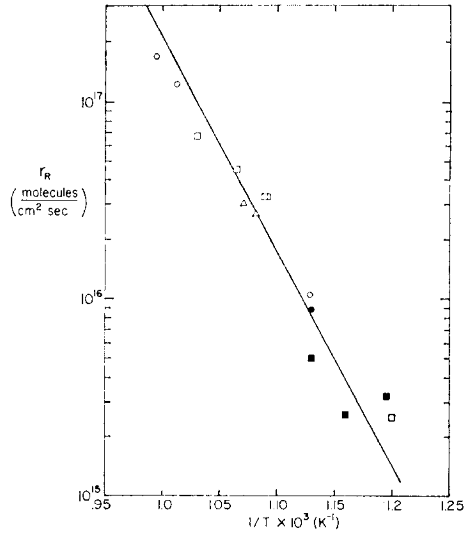

FIG. 3. Plot of r_R versus $1/T$ for the low temperature, zero-order regime. The slope of this line gives E_R = 49,600 cal/mole.

At 950 K, the order of the reaction decreases from unity to zero order with increasing pressure. These data and our previous study of this reaction on Pt (*1*) suggest that a Langmuir–Hinshelwood rate expression

$$r = k_R\theta_{NH_3} = \frac{k_R K_{NH_3} P_{NH_3}}{1 + K_{NH_3} P_{NH_3}} \qquad (3)$$

should correlate these results. The reaction rate constant k_R and the adsorption constant K_{NH_3} should have Arrhenius forms

$$k_R = k_{0R} \exp[-E_R/RT] \qquad (4)$$

and

$$K_{NH_3} = K_{0NH_3} \exp[(E_d - E_a)/RT] \qquad (5)$$

with E_R, E_d, and E_a the activation energies of reaction, desorption, and adsorption, respectively. Figure 3 shows a plot of log r_R versus $1/T$ for the low temperature portions of the curves which exhibit zero-order kinetics, and Fig. 4 shows log r_R/P_{NH_3} versus $1/T$ in the high temperature, first-order regime.

The slopes and intercepts of these lines give

$$k_R \text{ (molecules } cm^{-2}\ sec^{-1}) = 1.57 \times 10^{28} \exp[-49{,}600/RT] \qquad (6)$$

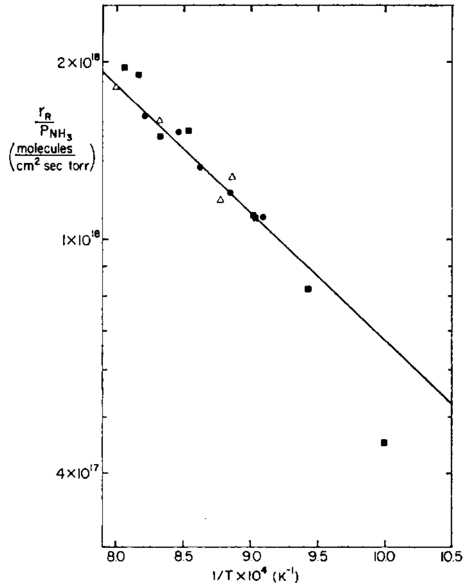

FIG. 4. Plot of r_R/P_{NH_3} versus $1/T$ for the high temperature, first-order regime. The slope of this line gives $E_R - E_{NH_3} = 10{,}000$ cal/mole.

and

$$K_{NH_3}\ (\text{Torr}^{-1}) = 6.7 \times 10^{-9} \exp[39{,}600/RT]. \quad (7)$$

The solid curves drawn through data points in Figs. 1 and 2 are those *calculated* from Eq. 3 with parameters from Eqs. 6 and 7. Deviations of up to 40% are observed at 0.050 Torr and low temperatures, but except for these measurements near the lowest observable rates, no data points differ from the LH rate expression by more than 20% for a pressure range of a factor of 25 and for rates varying by a factor of 10^3.

We also searched for discontinuities in the rate in crossing the Curie or α–γ transition temperatures, but none were observed within the limits of detectability.

Hydrogen Promotion

Rates were also measured in mixtures of NH_3 and H_2 to determine the influence of H_2 on the decomposition rate. Figures 5 and 6 show r_R versus T for $P_{NH_3} = 0.65$ and 0.30 Torr, respectively. Similar sets of data were obtained for $P_{NH_3} = 0.1$ and 0.25 Torr for hydrogen pressures between 0.070 and 1 Torr. Under these conditions,

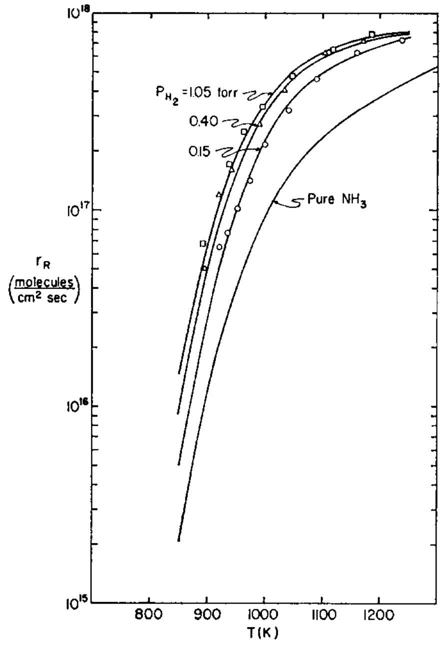

FIG. 5. Plot of r_R versus T for $P_{NH_3} = 0.65$ Torr with hydrogen pressures indicated. The rate is enhanced by hydrogen but becomes independent of P_{H_2} at high pressures.

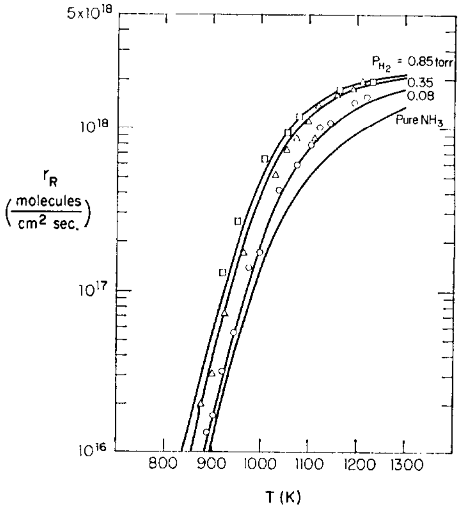

FIG. 6. Plot of r_R versus T for $P_{NH_3} = 0.3$ Torr with hydrogen pressures indicated. The rate is enhanced by hydrogen but becomes independent of P_{H_2} at high pressures.

the rate of reaction is *always enhanced by hydrogen.* Figure 7 shows the ratio of reaction rates with and without added H_2 as a function of P_{H_2} for two ammonia pressures. On Pt at low temperatures hydrogen inhibits the decomposition rate by competitive adsorption (*1*), and most investigators (*6*) have reported hydrogen inhibition on promoted Fe at low temperatures. Logan, Moss, and Kemball (LMK) (18) observed promotion on Fe films and suggested that their data and the hydrogen enhancement reported earlier by Love and Emmett (*19*) on singly promoted Fe could be explained by assuming reaction on Fe in hydrogen but on iron nitride in the absence of hydrogen,

$$r = k_{Fe}\theta_{Fe}\theta_{NH_3} + k_{nitride}\theta_{nitride}\theta_{NH_3}, \qquad (8)$$

with k_{Fe} and $k_{nitride}$ the rate constants of the reaction on Fe and nitride, respectively, and $\theta_{Fe} = 1 - \theta_{nitride}$. They postulated that there should be an equilibrium reaction between iron and nitride, Eq. 2, and, letting θ_{Fe} represent the fraction of the surface which is free of iron, and $\theta_{nitride}$ represent the fraction which is iron nitride, the equilibrium constant of Eq. 2 may be written

$$K_N = \frac{P_{H_2}{}^3}{P_{NH_3}{}^2}\left(\frac{\theta_{nitride}}{\theta_{Fe}}\right)^2. \qquad (9)$$

Using this idea, we shall develop an expression for the rate versus P_{NH_3} and P_{H_2} and use it to analyze our results. Equation (8) becomes

$$r = k_{Fe}\theta_{Fe}\frac{K_{NH_3}^{Fe}P_{NH_3}}{1 + K_{NH_3}^{Fe}P_{NH_3}} + k_{nitride}\theta_{nitride} \times \frac{K_{NH_3}^{nitride}P_{NH_3}}{1 + K_{NH_3}^{nitride}P_{NH_3}}, \qquad (10)$$

where $K_{NH_3}^{Fe}$ and $^{nitride}_{NH_3}$ are the adsorption constants on clean and nitrided surfaces.

If these adsorption constants for NH_3 are the same on both surfaces, Eqs. 9 and

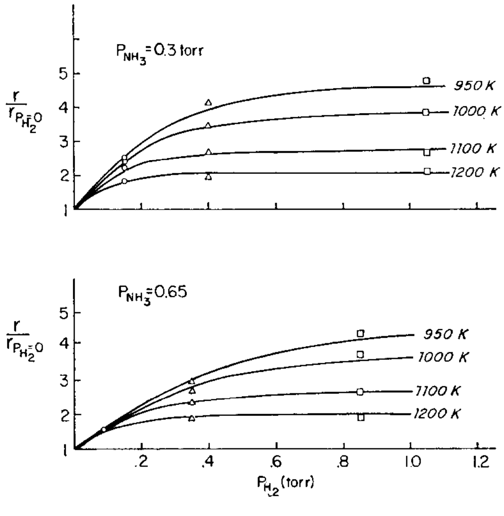

FIG. 7. Plot of the ratio of rates with and without added hydrogen versus P_{H_2}. These curves show that the rate becomes insensitive to P_{H_2} and that the enhancement of hydrogen is reduced as the temperature increases.

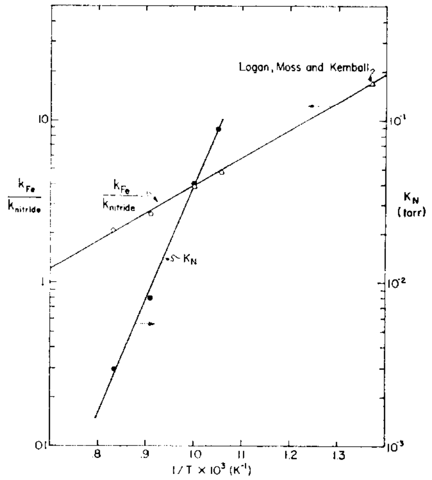

FIG. 8. Plots K_N, defined by Eq. 9, and the ratio of rates with and without added hydrogen versus $1/T$ using data from Fig. 7. This gives K_N, the equilibrium constant for nitride formation, indicated in Eq. 14. The ratio of rate constants with and without hydrogen obtained by Logan, Moss, and Kenball (ref. *18*) lies on the line drawn through our data.

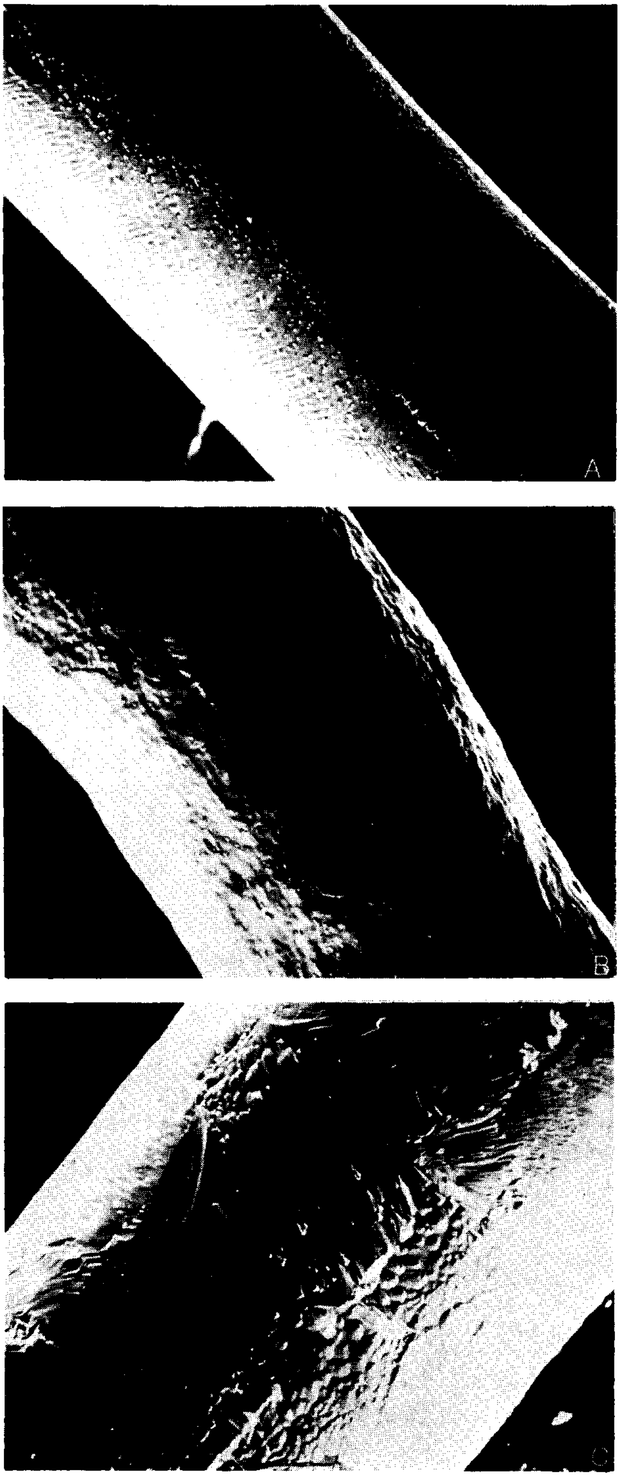

FIG. 9. Scanning electron micrographs of 0.025-cm-diameter Fe wires after heating in NH_3 at 0.5 Torr for 2 hr. Areas of all wires are close to geometric areas. (a) Heated in vacuum (5×10^{-7} Torr) without temperature cycling; (b) heat in vacuum with temperature cycling; (c) heated in pure NH_3 without temperature cycling; (d) heated in pure NH_3 with temperature cycling; (e) heated in NH_3 with 1 Torr of H_2 added without cycling; (f) heated in NH_3 with 1 Torr of H_2 added with cycling.

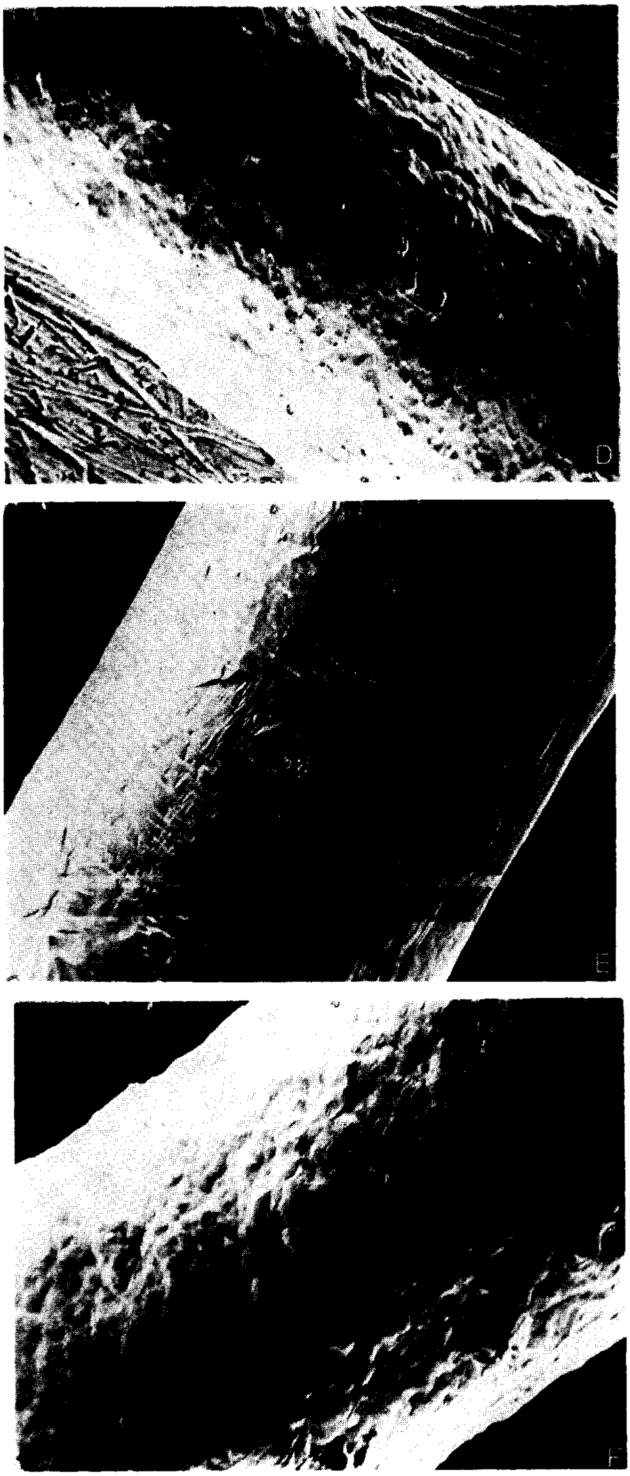

FIGURE 9—(*continued*)

10 may be combined to obtain

$$r_R = \left[1 + \frac{\dfrac{k_{\mathrm{Fe}}}{k_{\mathrm{nitride}}} - 1}{1 + K_{\mathrm{N}}^{\frac{1}{2}} \dfrac{P_{\mathrm{NH_3}}}{P_{\mathrm{H_2}}^{\frac{3}{2}}}} \right] \times \frac{k_{\mathrm{nitride}} K_{\mathrm{NH_3}} P_{\mathrm{NH_3}}}{(1 + K_{\mathrm{NH_3}} P_{\mathrm{NH_3}})}. \quad (11)$$

Clearly, the rate expression reduces to Eq. 3 when $P_{\mathrm{H_2}}^{\frac{3}{2}} \ll K_{\mathrm{N}}^{\frac{1}{2}} P_{\mathrm{NH_3}}$. When $P_{\mathrm{H_2}}^{\frac{3}{2}} \gg K_{\mathrm{N}}^{\frac{1}{2}} P_{\mathrm{NH_3}}$, then

$$r_R = \frac{k_{\mathrm{Fe}} K_{\mathrm{NH_3}} P_{\mathrm{NH_3}}}{1 + K_{\mathrm{NH_3}} P_{\mathrm{NH_3}}} \quad (12)$$

and the rate again becomes independent of $P_{\mathrm{H_2}}$.

The ratio of rates with and without hydrogen should be temperature dependent if the activation energies for the reaction on Fe and nitride are different. Figure 8 shows an Arrhenius plot of data in Figs. 5 and 6. From this plot we obtain

$$\frac{k_{\mathrm{Fe}}}{k_{\mathrm{nitride}}} = 7.55 \times 10^{-2} \exp\left(\frac{7900}{RT}\right). \quad (13)$$

Next, we substitute Eq. 13 in Eq. 12, and from experiments at $P_{\mathrm{H_2}} = 0.15$ and 0.4 Torr in Fig. 5, we obtain K_{N} as a function of T. From an Arrhenius plot for K_{N} (shown in Fig. 8) we obtain

$$K_{\mathrm{N}} = 8.14 \times 10^{-9} \times \exp\left(\frac{30{,}500}{RT}\right)(\mathrm{Torr}). \quad (14)$$

The curves drawn through data points in Figs. 5–7 are those calculated using these parameters in the above reaction rate expression.

Surface Morphology

The rates just described require a knowledge of the surface area to determine k_{0R} which is proportional to area. From SEM micrographs it was established that, while repeated cycling of the wire temperature in $\mathrm{NH_3}$ or pretreatment in $\mathrm{O_2}$ produced alterations in surface structure, surfaces on which kinetics were determined retained geometric areas to within the accuracy of the rate measurements.

SEM micrographs showed that extensive facetting and distinct circular regions of a different composition occurred upon heating and especially upon temperature cycling in $\mathrm{NH_3}$. Figures 9 and 10 show Fe surfaces which had been heated continuously at 1200 K (9a, c, and e) and with temperature cycling between 300 and 1200 K (9b, d, and f) in vacuum at ~3×10^{-7} Torr (9a and b), in $\mathrm{NH_3}$ at 0.5 Torr (9c and d), and in 0.5 Torr of $\mathrm{NH_3}$ plus 1.0 Torr of $\mathrm{H_2}$ (9e and f). The total time of heating of each wire was ~4 hr and cycled wires went through 50–100 temperature cycles.

It is evident from Fig. 9a, c, and e that heating continuously in vacuum produces only slight alterations while in $\mathrm{NH_3}$ or $\mathrm{NH_3} + \mathrm{H_2}$ extensive facetting of crystal planes and etching of grain boundaries occurs. Similar results have been reported previously (*20*), and analogous behavior is observed on Pt (*21*), although etching is much more rapid on Fe.

Temperature cycling causes much more extensive roughing and leaves a surface on which neither flat facets nor grain boundaries are evident. Temperature cycling in pure $\mathrm{NH_3}$ produces dark circular regions in some areas of the wire as shown in Fig. 9d and in Fig. 10a and b. Sizes of these regions range from the 300 Å limit of detectability to 10,000 Å. While it was difficult to determine structures precisely for these sizes, we believe that most of these structures are a separate phase rather than being pits, because higher magnification micrographs yield images from the dark regions, and rounded pit mouths are not observed. There appeared to be electron beam damage of these structures and some

TABLE 1

Langmuir–Hinshelwood Parameters for NH_3 Decomposition on Pt and Fe

Surface	k_{0R} $\left[\frac{\text{molecules}}{\text{cm}^2\ \text{sec}}\right]$	E_R (cal/mole)	K_{0NH_3} (Torr^{-1})	E_{NH_3} (cal/mole)	K_{0H_2} (Torr$^{-1.5}$)	E_{H_2} (cal/mole)
Pt	2.27×10^{23}	21,000	4.35×10^{-5}	16,800	9.8×10^{-6}	27,700
Fe($P_{H_2} = 0$)	1.57×10^{28}	49,600	6.7×10^{-9}	39,600	—	—
Fe($P_{H_2} \gg 0$)	1.19×10^{27}	41,700	6.7×10^{-9}	39,600	—	—

indication that they decomposed with time to yield pits. When wires were cut and their ends examined, similar dark regions were observed throughout the wire.

Figure 10d shows a wire which had been heated in O_2 and then cycled even more extensively in NH_3 at higher pressures and at various temperatures. The wire had decreased in length by ~20%, and in the SEM micrograph the surface appears to have been compressed axially to produce an almost pleated surface. Distinct large holes are also evident.

Cycling across the α–γ phase transition induces a visible motion of the wire, and resultant stresses in the wire evidently produce the observed changes. Recrystallization of Fe to produce smaller grains upon crossing the α–γ transition temperature has been noted. In the absence of H_2, nitride should form more rapidly, but, as discussed previously, nitrides should be stable only at low temperatures. We suggest that the dark circular regions on the wires cycled in NH_3 may be metastable nitride nucleated along line defects created by the phase transition. Nitride formation at dislocations and grain boundaries has been studied at low temperatures (*14*) as has the formation of pockets of nitrogen when iron containing nitrogen is solidified (*16*).

When the wire was heated in O_2 for 15 min at 0.2 Torr and then heated in NH_3, the rate of NH_3 decomposition followed the same rate versus temperature curve as on the unoxidized wire but the rate was uniformly higher by a factor of ~6 at all temperatures. Figure 10c shows that this pretreatment produces an oxide layer which, when reduced in NH_3, contains cracks and does not adhere to the core. (The wire in Fig. 10c had been intentionally bent to remove a portion of the surface layer). The increased rate on an oxygen-treated surface is therefore consistent with increased iron surface area produced by treatment in O_2 followed by reduction of the oxide in NH_3.

DISCUSSION

Kinetics

As on Pt, we find that the kinetics of NH_3 decomposition can be fit quantitatively to the LH unimolecular rate expression. On Pt, hydrogen inhibited the reaction at low temperature as expected for competitive adsorption

$$r_R = \frac{k_R K_{NH_3} P_{NH_3}}{1 + K_{NH_3} P_{NH_3} + K_H P_{H_2}{}^{\frac{1}{2}}}, \qquad (15)$$

whereas on Fe the rate was enhanced by H_2 until it approached a new value independent of P_{H_2}. The assumption of nitride formation in NH_3 but not with high pressures of H_2 leads to a rate expression consistent with the experimental results (Eq. 11), but we regard this fit as in no sense unique. Because of increased scatter in the data with added H_2, the fits to the data from Eqs. 11 and 3 shown in Figs. 5 and 6 could not be used to obtain K_{NH_3} with and without H_2 independently, but instead the adsorption constant was as-

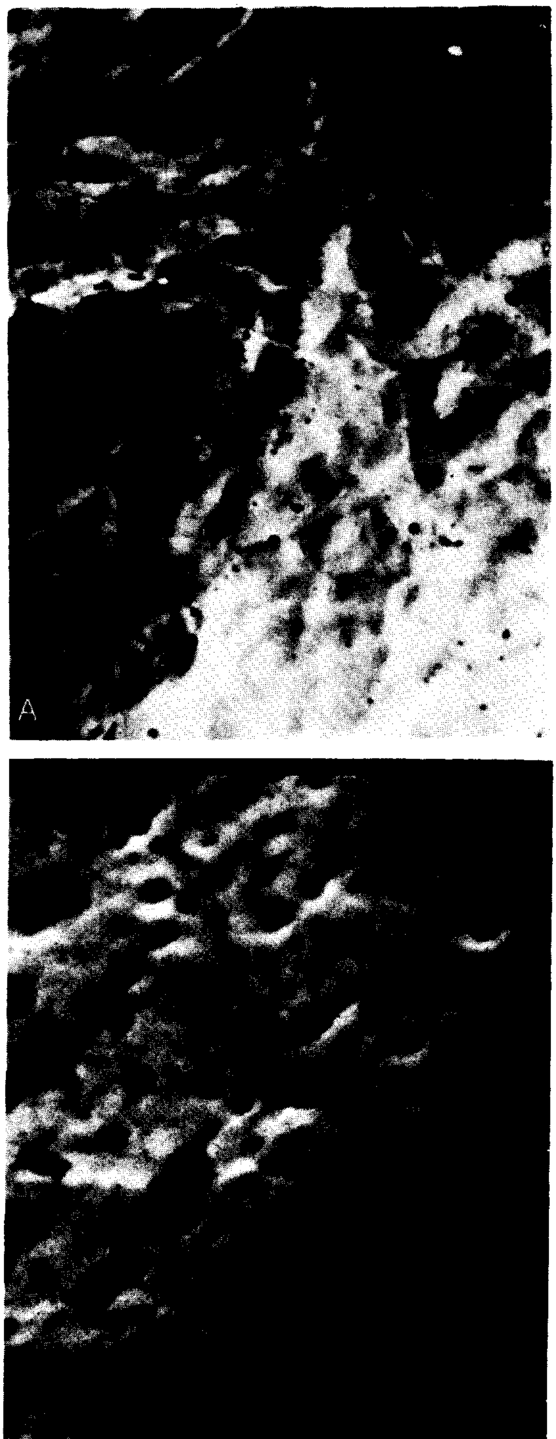

FIG. 10. Scanning electron micrographs of iron wires at higher magnification, (a) and (b), and after first heating in O_2 before reduction in NH_3, (c) and (d). Micrographs (a) and (b) are after heating in NH_3 with cycling at magnifications of 3 and 9 times those in Fig. 9 and show that the surfaces contain small dark circular regions believed to be nitride formed at line effects induced by temperature cycling. Micrographs (c) and (d) show that the surface area is considerably enhanced by oxidation and reduction.

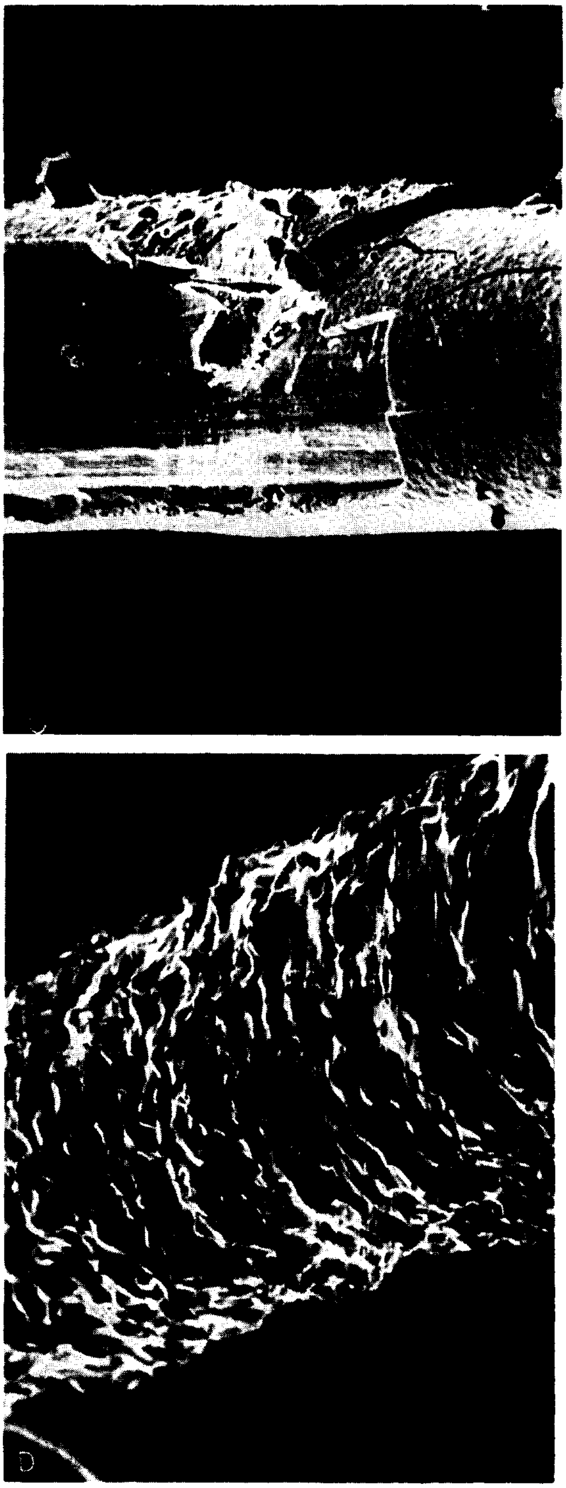

FIGURE 10—*(continued)*

sumed to be independent of P_{H_2}. However, this variation is probably not large.

In Table 1 are summarized the adsorption and reaction parameters on Fe with and without hydrogen (presumably on clean Fe and on nitride) and on polycrystalline Pt. The rate on Pt, indicated by the dashed lines in Fig. 1 for $P_{NH_3} = 0.1$ Torr and 1.2 Torr, is higher than on Fe up to ~1200 K, and the rate on Fe depends much more strongly on temperature than it does on Pt. This is expected for the higher activation energy of reaction and higher heat of adsorption on Fe. The adsorption preexponential factors K_{0NH_3} for localized adsorption of a nondissociated species should be

$$K_{0NH_3} = \frac{s_0}{\nu_0(2\pi MRT)^{\frac{1}{2}}} \simeq 10^6 \frac{s_0}{\nu_0} \text{ (Torr}^{-1}) \quad (16)$$

and for estimates of the initial sticking coefficient s_0 as $10^{-1\pm1}$ and the desorption preexponential factor ν_0 as $10^{13\pm1}$ sec^{-1}, we obtain $10^{-10} < K_{0NH_3} < 10^{-6}$ Torr^{-1}. Thus, our measured adsorption constants are within their "normal" range on both surfaces.

Comparison of the rate in the first-order regime with the NH_3 flux to the surface yields a reaction probability at 800 K and 1 Torr of $\sim 10^{-3}$ on Pt and $\sim 10^{-5}$ on Fe without added H_2 and $\sim 10^{-4}$ with high pressures of H_2. The highest measured reaction probabilities (fractions of incident NH_3 fluxes which react) were $\sim 5 \times 10^{-3}$ on both surfaces.

There should of course be a hydrogen inhibition term on Fe due to competitive adsorption with a form similar to Eq. 15. However, the heat of adsorption of NH_3 on Fe appears to be so high (Table 1) that it is reasonable that H_2 inhibition on Fe should only be observed at lower temperatures and higher pressures than employed here.

Little comparison with previous studies of decomposition kinetics on Fe is possible because most used promoted and supported Fe at lower temperatures and higher NH_3 and H_2 pressures with narrower ranges of these variables than employed here. As summarized by Bond (*6*) most investigators obtain activation energies between 40 and 55 kcal/mole, in good agreement with our low temperatures value of 49,600 cal/mole. The order with respect to NH_3 is typically near unity while ours is independent of P_{NH_3} for these conditions. Hydrogen inhibition as $P_{H_2}^{-1.5}$ is common at low temperatures, while we observe only promotion. Few investigators have specified surface area or reactor conditions sufficiently to permit comparison of rates per unit area.

Our results are in good agreement with Love and Emmett (*19*) on singly promoted Fe and with Logan, Moss, and Kemball (*18*) on Fe films. Love and Emmett obtained $r_R \sim P_{H_2}^{1.2} P_{NH_3}^{-0.8}$ and our expression, Eq. 11, can give $r_R \sim P_{H_2}^{1.5} P_{NH_3}^{-1}$ for suitable choices of parameters. Extrapolation of our rate expression down to 680 K yields a rate of 1.5×10^{13} molecules cm^{-2} sec^{-1} versus the LMK rate of 1.7×10^{12}, but the expected H_2 inhibition at low temperatures could easily account for this difference. LMK also observed different rates with and without H_2 and reported a rate constant ratio $k_{Fe}/k_{nitride}$ of 17 at 728 K. This point, shown in Fig. 8, lies on the line drawn through our data.

It appears likely that the decomposition rate on Fe and singly promoted (supported) Fe is different than on doubly promoted (added K_2O) Fe, and our high temperatures certainly reduce possibilities for complex surface structures such as nitrides. However, there is no need to invoke Temkin–Pyzhev kinetics to explain our results, and most previous results appear to be reasonably consistent with our rate expressions, power law expressions giving adequate representations of the rate over limited ranges of temperature and pressure. Effects of crystallographic averaging and multiple bonding states do not produce measurable deviations from the LH rate expression, and our recent results on this reaction on single crystal planes of Pt (*5*) show that, while rates vary by more than a factor of 10, this produces only an altered effective surface area in the homogeneous surface assumption for a polycrystalline surface.

As with Pt we conclude that it is impossible, even with extensive and accurate reaction rate measurements and an apparently unique rate expression, to determine reaction mechanisms in the sense of specifying rate-limiting steps or active complexes from kinetics alone.

Surface Nitride

Following LMK, we have interpreted the difference in rates with and without hydrogen as reaction on a surface nitride in the absence of added hydrogen. However, while they demonstrated by X-ray analysis the existence of nitride on their films at low temperature, our measurements indicate the absence of significant bulk nitrides at our higher temperatures. This leaves the possibility of a "surface nitride," some form of adsorbed and dissolved nitrogen near the surface. This was also inferred by LMK to explain some of their rate variations when bulk nitride was not detected. Roginskii *et al.* (*20*) also suggested the formation of a "surface nitride" on iron surfaces heated in ammonia. Such a state near the surface could be thermodynamically stable in the reacting system even though bulk nitrides do not form. Since the rate increases with P_{H_2} for small hydrogen pressures (Fig. 7), this implies that the nitride is one of variable composition, i.e., in dissolved nitrogen rather than a distinct nitride phase of fixed composition. This assumption is supported by the work of Schmidt (*22*) who observed ions type $FeN_xH_n^+$ ($x \geq 2$) using field ion mass spectroscopy from an iron field emitter in an NH_3 atmosphere. Other indirect evidence on surface nitride formation has been cited by Robertson (*23*).

The often repeated assumption that nitrogen desorption is the rate limiting step in NH_3 decomposition on Fe seems to be based primarily on the fact that the activation energy of decomposition of Fe_4N is very close to that measured for NH_3 decomposition on Fe (*18*). Nitride (if that is the species present in the absence of hydrogen) does in our results produce a lower rate compared to the high hydrogen pressure situation. However, nitrogen adsorbs only weakly (or slowly) on Fe, and, at high temperatures where desorption of bulk nitrides as N_2 is rapid, there may be no nitrogen on the surface which is not in the form of NH_3 or its residues.

It is impossible to decide the chemical composition of the surface or the adsorbed complexes from kinetics alone, and further speculation on the nature of the alterations in the surface seems unwarranted, especially since direct spectroscopic and elemental analysis of surfaces during catalytic reactions should be obtainable in the near future.

SUMMARY

Our rates of NH_3 decomposition on Fe require only the LH unimolecular rate expression for their complete description, although a different reaction rate parameter k_R must be used at high hydrogen pressures. Our temperature range, while extensive, does not overlap that typically used for this reaction, and the reaction may be more complicated at lower temperatures. However, in the absence of chemical promotors, kinetics at low temperatures appear to be consistent with our rate expression, although we do not observe the hydrogen inhibition which should be important only at low temperatures.

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REFERENCES

1. Löffler, D. G., and Schmidt, L. D., *J. Catal.* **41**, 440 (1976).
2. Pignet, T. P., and Schmidt, L. D., *Chem. Eng. Sci.* **29**, 1123 (1974).
3. Hori, G. K., and Schmidt, L. D., *J. Catal.* **38**, 335 (1975).
4. Pignet, T. P., and Schmidt, L. D., *J. Catal.* **40**, 212 (1975).
5. Löffler, D. G., and Schmidt, L. D., *Surface Sci.*, to be published.
6. Bond, G. C., "Catalysis by Metals," Academic Press, New York, 1962.
7. Temkin, M., and Pyzhev, V., *Acta Phys.* **12**, 327 (1940).
8. Ozaki, A., Taylor, H., and Boudart, M., *Proc. Roy. Soc. Ser.* A **258**, 47 (1960).
9. Mardaleishuili, R. E., Hu, S.-C., Zh. Y. Smorodinskaya, O., *Zh. Ya. Kinetika i Kataliz* **8**, 664 (1967) (English translation).
10. Takezawa, N., and Mexaki, R., *Canad. J. Chem. Eng.* **48**, 428 (1970).
11. Boudart, M., Delbouille, A., Dumesic, J., Khammouma, S., and Topsoe, H., *J. Catal.* **37**, 486 (1975).
12. Dumesic, J. A., Topsoe, H., Khammouma, S., and Boudart, M., *J. Catal.* **37**, 503 (1975).
13. Grabke, H. J., *Ber. Bunsenges. Phys. Chem.* **72**, 533 (1968).
14. Keh, A. S., and Wriedt, H. A., *Trans. Met. Soc. AIME* **224**, 560 (1962).
15. Lotz, C. R., and Sebba, F., *Trans. Faraday Soc.* **53**, 1246 (1957).
16. Fast, J. D., "Interaction of Metals and Gases," Academic Press, New York (1965).
17. Fast, J. D., "Interaction of Metals and Gases," Vol. 2, Macmillan, London, 1971.
18. Logan, S. R., Moss, R. L., and Kemball, C., *Trans. Faraday Soc.* **54**, 922 (1958).
19. Love, K., and Emmett, P., *J. Amer. Chem. Soc.* **63**, 3297 (1941).
20. Roginskii, S. Z., Tretýakov, J. I., and Shekhter, A. B., *Dokl. Akad. Nauk SSSR* **91**, 881 (1953).
21. McCabe, R., Pignet, T., and Schmidt, L. D., *J. Catal.* **32**, 114 (1974).
22. Schmidt, W. A., *Angew. Chem.* **80**, 151 (1968).
23. Robertson, A. J. B., "Catalysis of Gas Reactions by Metals," Logos Press Limited, London, 1970.