

Kinetics of Ammonia Decomposition on Nickel

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Two kinetic regimes were observed in the decomposition of NH_3 over nickel wires at temperatures between 750 and 1350K and NH_3 pressures between 5.3 and 133 Pa. At temperatures below 1000K, the decomposition is highly activated ($211 \pm 20 \text{ kJ mol}^{-1}$), and the rate is independent of NH_3 pressure. Above 1000K a transition to first-order kinetics occurs as the apparent activation energy decreases with increasing temperature. The data were closely predicted by a rate expression which was derived from an analysis of the elementary reaction steps involved in NH_3 decomposition. The analysis of the data indicates that the desorption of strongly adsorbed nitrogen is the rate-controlling step in the zero-order regime, and the adsorption of NH_3 is the rate-controlling step in the first-order regime.

INTRODUCTION

Nickel has been shown to be effective for the conversion of nitric oxide in laboratory feedstreams designed to simulate sulfur-free and oxygen-deficient automobile exhaust. Klimisch and Taylor (1) studied the reactions between NO and H_2 over catalysts containing copper and nickel supported on alumina. Copper was found to promote the reduction of nitric oxide to NH_3 and nickel was found to be effective in decomposing NH_3 to nitrogen and hydrogen. Although recent "three-way" automotive exhaust catalysts have utilized rhodium for the control of nitric oxide emissions, nickel and other nonnoble transition metals are of interest as potential supplements or replacements for rhodium (2). Rhodium has been found to produce high yields of NH_3 from nitric oxide reduction in simulated automotive exhaust which is highly reducing (3). Taylor (4) has suggested that nickel might be a useful additive to rhodium-containing "three-way" catalysts for decreasing NH_3 emissions during transient operation in the fuel-rich regime.

Only a few studies of NH_3 decomposition on nickel have been reported. Logan and Kemball (5) examined the decomposition of NH_3 on evaporated metal films of nickel in

H_2 - NH_3 mixtures containing high ratios of H_2 to NH_3 . They concluded that the desorption of nitrogen is the rate-limiting step in the reaction and that the reaction occurs with an activation energy of $\sim 180 \text{ kJ mol}^{-1}$ over the temperature range 663-773K. Tammaru *et al.* (6) examined the decomposition of NH_3 over an unsupported nickel catalyst at 573K. They concluded that the rate-limiting step in the decomposition is the desorption of nitrogen. A similar conclusion was reached by Kazusaka (7) in a study of NH_3 decomposition over unsupported nickel using isotope techniques.

EXPERIMENTAL

The NH_3 decomposition experiments were carried out over resistively heated nickel wires in flowing NH_3 at pressures between 5.3 and 133 Pa (0.04 to 1.0 Torr). The reactor is a six-way cross (type 304 stainless steel) of 800 cm^3 volume. A vacuum feedthrough with two 0.24-cm-diameter copper leads was used to support and heat the nickel wire samples. Data were obtained on two wire samples (Materials Research Corporation MARZ grade)—one of 0.025-cm-diameter by 1.6 cm in length and the other of 0.05-cm-diameter by 8 cm in length. Rates measured on the two wires under identical reaction conditions differed

by no more than 30%. The wire temperatures were measured with a 0.0075-cm-diameter chromel–alumel thermocouple spot-welded near the middle of the wire. Short pieces of 0.013-cm-diameter nickel wire were welded between the nickel wire sample and the support rods in order to minimize heat losses by conduction and assure uniform sample temperature.

Experiments were carried out by leaking ammonia (99.998% NH_3) from glass storage bulbs into the reactor. Flow rates were determined from the rate of decrease of the pressure in the glass bulbs. Capacitance manometers were used to measure the pressure in both the glass bulbs and the reactor. Gases were continuously pumped from the reactor using a mechanical vacuum pump which was isolated from the reactor with a liquid-nitrogen trap. The pressure in the reactor was controlled by adjusting the conductance of the pumping system with a valve mounted on the reactor outlet port. A turbomolecular-pumped high-vacuum chamber (base pressure of 10^{-7} Pa) was located adjacent to the reactor. The high-vacuum chamber contained an ion gauge and quadrupole mass spectrometer. A leak valve was located between the reactor and the chamber containing the mass spectrometer. The leak rate was adjusted to provide a pressure of 10^{-5} Pa (measured with the ion gauge) in the mass spectrometer chamber. Steady-state conversions were determined by monitoring the production of N_2 with the mass spectrometer. The mass spectrometer was calibrated by flowing a mixture of 5% N_2 in NH_3 through the reactor under conditions of no reaction (i.e., over the cold nickel wire) and measuring the $m/e = 28$ mass spectrometer signal with a total pressure of 10^{-5} Pa in the high-vacuum chamber. The calibration procedure was carried out prior to each set of rate measurements at a given reactor pressure.

In some experiments, steady-state conversions of NH_3 were determined both from the production of N_2 and from the disap-

pearance of NH_3 . Close agreement was obtained between the two methods, which indicates that only negligible amounts of the NH_3 , if any, decomposed to bulk nickel nitride and hydrogen. Bulk nitrides of nickel have been reported (23) but little effort has been directed toward determining their stabilities as a function of temperature and partial pressures of NH_3 and H_2 . Although we cannot rule out the possibility that bulk nitrides of nickel may be stable under some of the conditions encountered in these experiments, we saw no evidence of either changes in the appearance of the samples or changes in the rate data with reaction time to suggest that bulk nickel nitride was formed during the course of these experiments.

Reaction rates were calculated under steady-state reaction conditions at conversions less than 10% using the stirred-tank reactor equation

$$r_i = \frac{Q}{ART_g} (P_i^0 - P_i), \quad (1)$$

where, in general, r_i is the reaction rate of species i , Q is the volumetric flow rate (at reactor conditions), A is the sample area, R is the gas constant, T_g is the temperature of the gas in the reactor, and P_i^0 and P_i are the partial pressures of species i in the reactor associated with the feed and with the steady-state reaction mixture, respectively.

The stirred-tank reactor equation is applicable under conditions where the rate of mass transfer of molecules to and from the wire is large compared to the rate of reaction at the wire surface. Loffler and Schmidt (8) have calculated rates between 10^{20} and 10^{21} molecules $\text{cm}^{-2} \text{s}^{-1}$ for the transport of small molecules to wire surfaces at pressures above 133 Pa. The highest rate observed in our study was $\sim 4 \times 10^{18}$ molecules $\text{cm}^{-2} \text{s}^{-1}$, which was obtained at 1350K in both pure NH_3 (133 Pa) and in mixtures of NH_3 (133 Pa) and Ar (399 Pa) (Fig. 1).

The nickel wires were heated in 80 Pa hydrogen (99.9995% H_2) at temperatures in

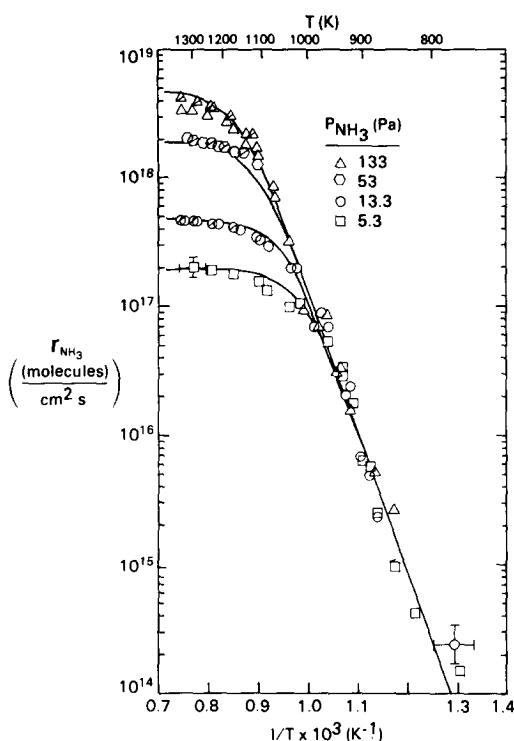


FIG. 1. Ammonia decomposition rate as a function of inverse temperature on nickel wires for different NH_3 pressures. Open symbols represent experiments carried out in pure NH_3 . Symbols with diagonal lines represent experiments carried out in NH_3 -Ar mixtures. The curves were calculated from Eq. (3) using parameter values given in Table 1.

excess of 1300K for 1 hr prior to obtaining the rate data. This treatment led to reproducible NH_3 decomposition rates. One sample was removed from the reactor after heating in H_2 and was transferred to a surface analysis chamber containing an Auger electron spectrometer (AES). The AES analysis showed the absence of sulfur and foreign metals on the nickel surface.

RESULTS AND DISCUSSION

Rates of NH_3 decomposition are shown in Fig. 1 as a function of inverse temperature for NH_3 pressures between 5.3 and 133 Pa. The open symbols represent experiments carried out in pure NH_3 while the symbols containing diagonal lines represent

experiments carried out in NH_3 -Ar mixtures.

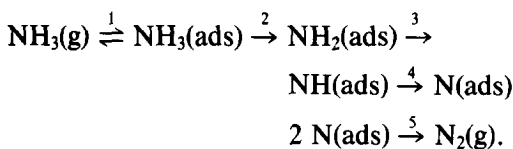
Figure 1 shows the rate of NH_3 decomposition to be independent of pressure for temperatures below 1000K. At higher temperatures the order of the pressure dependence increases until it is nearly first order at temperatures above 1300K. The transition from zero-order to first-order dependence upon ammonia pressure is accompanied by a decrease in the apparent activation energy from $211 \pm 20 \text{ kJ mol}^{-1}$ to less than 25 kJ mol^{-1} at temperatures in excess of 1300K (less than 15 kJ mol^{-1} for ammonia pressures of 53 Pa or less).

The change in reaction order from zero at low temperatures and/or high pressures to nearly one at high temperatures and/or low pressures is characteristic of unimolecular Langmuir-Hinshelwood (L-H) kinetics (9). However, analysis of the data by L-H kinetics yields a value of at least $186 \pm 20 \text{ kJ mol}^{-1}$ for the average heat of adsorption of NH_3 on nickel. This is two to three times greater than the heats of adsorption indicated from thermal desorption studies of NH_3 on Ni(111) (10, 11) and Ni(110) (12). Thus the assumption of equilibrium between gaseous and adsorbed NH_3 does not appear to be valid under the conditions of this study.

An alternative model is suggested from the observation that the apparent activation energy of $211 \pm 20 \text{ kJ mol}^{-1}$, measured for the zero-order reaction regime, is consistent with activation energies of 180 to 218 kJ mol^{-1} reported for the desorption of strongly adsorbed nitrogen atoms, as N_2 , from nickel single-crystal surfaces (13-16). The rate-limiting step in the zero-order kinetic regime may, therefore, be the desorption of nitrogen. Grunze *et al.* (17) have shown from a photoemission study of NH_3 on Ni(110) that decomposition of NH_3 proceeds by the sequential dissociation of adsorbed NH_3 to atomic nitrogen. The following sequence of reaction steps can, therefore, be written to describe NH_3 decomposition:

TABLE 1
Rate Parameters for NH₃ Decomposition on Nickel

Parameter	Functional form	Parameter value
k_{-1}	$k_{-1}^0 \exp(-E_{-1}/RT)$	$k_{-1}^0 = 1 \times 10^{13} \text{ s}^{-1}$ $E_{-1} = 79.5 \text{ kJ mol}^{-1}$
k_1	$S_0(2\pi MRT_p)^{-1/2}$	$S_0 = 0.011$ $(2\pi MRT_p)^{-1/2} = 3.7 \times 10^{18}$ molecules $\text{cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$
k_2	$k_2^0 \exp(-E_2/RT)$	$k_2^0 = 1 \times 10^{13} \text{ s}^{-1}$ $E_2 = 56.5 \text{ kJ mol}^{-1}$
k_5	$k_5^0 \exp(-E_5/RT)$	$k_5^0 = 1 \times 10^{13} \text{ s}^{-1}$ $E_5 = 211 \text{ kJ mol}^{-1}$
n_0		$n_0 = 1.5 \times 10^{15} \text{ cm}^{-2}$ (average of the surface atom densities of (111), (110), and (100) Ni)



The desorption of adsorbed atomic nitrogen, as N₂, from nickel single-crystal surfaces has been shown to follow first-order kinetics (16). Thus the steady-state rate of NH₃ decomposition is given, from the reaction sequence above, by

$$r_{\text{NH}_3} = k_5[\text{N}(\text{ads})]. \quad (2)$$

If the assumption is made that N(ads) is the only species present on the surface in appreciable concentration under reaction conditions, then it follows from the mass conservation equation for N(ads) that

$$r_{\text{NH}_3} = \frac{k_1 k_2 P_{\text{NH}_3}}{(k_{-1} + k_2)} \cdot \frac{1}{1 + \frac{k_1 k_2 P_{\text{NH}_3}}{n_0 k_5 (k_{-1} + k_2)}}. \quad (3)$$

NH₃ decomposition rates were calculated from Eq. (3) using the parameter values given in Table 1. The calculated rates are shown as the curves in Fig. 1 and agree closely with the data. At low temperatures Eq. (3) was found to be closely approximated by

$$r_{\text{NH}_3} = n_0 k_5, \quad (4)$$

whereas at the highest temperatures of the study Eq. (3) was found to be closely approximated by

$$r_{\text{NH}_3} = k_1 P_{\text{NH}_3}. \quad (5)$$

The limiting-rate expressions indicate that the NH₃ decomposition rate is controlled by the rate of nitrogen desorption at low temperatures and by the rate of NH₃ adsorption at high temperatures.

The parameter values used in the calculations were obtained from the literature in the cases where data were available. The desorption activation energy for NH₃(ads) (E_{-1}) was estimated from thermal desorption peak temperatures reported by Madey *et al.* (10) and by Seabury *et al.* (11) for NH₃ on Ni(111). The activation energy for the decomposition of NH₃(ads) to NH₂(ads) (E_2) was estimated from the photoemission data of Grunze *et al.* (17) for NH₃ decomposition on Ni(110). As noted previously, the value of 211 kJ mol⁻¹ for E_5 was found to provide a good fit to the zero-order data and to be consistent with reported activation energies of 180 to 218 kJ mol⁻¹ for the desorption of strongly bound nitrogen from nickel single-crystal surfaces (13–16).

Preexponential factors of 10¹³ s⁻¹ were assumed for all of the rate processes occurring on the nickel surface. The sensitivity of the calculated rates to the choice of the preexponential factor was examined for k_2 by varying the preexponential factor k_2^0 between 10¹² and 10¹⁴ s⁻¹ (the activation energy E_2 was varied simultaneously in order to maintain agreement with the low-temperature NH₃ decomposition data of Grunze *et al.* (17)). The value assumed for k_2^0 had little effect on the rates predicted by Eq. (3) over the full range of temperatures and pressures.

The initial (i.e., low coverage) sticking coefficient S_0 given in Table 1 was chosen to provide the best fit of the calculated curves to the high-temperature NH₃ decomposition data. The calculated rate is only sensitive to the value of S_0 for wire temperatures greater than 1000 K since r_{NH_3}

$\sim n_0 k_5$ at lower temperatures. Adsorption of NH_3 on nickel surfaces has been examined primarily at temperatures of 150K or lower (10, 11, 17). Grunze *et al.* (17) reported a sticking coefficient of ~ 0.1 for NH_3 on Ni(110) at 120K. The adsorption of NH_3 on Ni(111) (10) and Ni(110) (17) at low temperatures has been shown to occur with constant sticking coefficient which is characteristic of adsorption through a precursor state. Precursor adsorption kinetics have been shown to be activated and to result in a decrease in sticking probability with increasing surface temperature for most adsorption systems (18, 19). Thus $S_0 \sim 0.01$ is a reasonable value for the high-temperature sticking coefficient.

In summary, rate data obtained for the decomposition of NH_3 on nickel wires were used to compare L-H kinetics with a kinetic model derived from the assumption that adsorbed nitrogen atoms are the predominant surface species under steady-state reaction conditions (adsorbed-nitrogen model). Both models predict the observed zero-order kinetics at low temperatures and first-order kinetics at high temperatures. However, the L-H analysis requires the assumption of an anomalously high value of the heat of NH_3 adsorption, whereas the model based on adsorbed nitrogen predicts the NH_3 decomposition data using parameter values which are consistent with literature data obtained from studies of the elementary reaction steps. The adsorbed-nitrogen model is consistent with observations made in earlier studies of NH_3 decomposition carried out over nickel films (5) and unsupported nickel (6, 7) at higher pressures and lower temperatures. Desorption of nitrogen was found to be the rate-limiting reaction step in those studies as is true of the present study in the zero-order reaction regime.

The analysis of the NH_3 decomposition data on nickel parallels that used by Ertl and Huber (20) to describe NH_3 decomposition on iron wires at an NH_3 pressure of 7×10^{-4} Pa and wire temperatures between 580

and 850K. They found the apparent activation energy of the reaction to decrease from 188 ± 20 kJ mol $^{-1}$ to nearly zero as the wire temperature was increased from 580 to 850K. Ertl and Huber proposed a rate expression which differs from Eq. (3) only by the absence of the estimated surface atom density, n_0 , which has been incorporated into Eq. (3) in order to express the NH_3 decomposition rate on the basis of geometric surface area. They associated the strongly adsorbed atomic nitrogen with a "surface nitride" species whose properties have been analyzed in detail in studies of nitrogen adsorption on iron surfaces (21, 22).

Subsequent to submitting this paper for publication, data were reported by Ertl and Rüstig (24) for NH_3 decomposition on a polycrystalline nickel foil at a pressure of 4×10^{-4} Pa (3×10^{-6} Torr). Their data are consistent with the data reported here for NH_3 decomposition at higher pressures. As a further test of our reaction model, we extended our calculations to 4×10^{-4} Pa using Eq. (3) and the parameter values of Table 1. The transition from zero-order to first-order kinetics is predicted to occur largely between 750 and 800K in agreement with the observation of Ertl and Rüstig.

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