

Decomposition of NH₃ on Pd and Ir Comparison with Pt and Rh

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Received 29 April 1996; accepted 24 October 1996

Abstract

The unimolecular decompositions of NH₃ on polycrystalline wires and foils of Pd and Ir are examined and compared with the corresponding ones on Pt and Rh. The reactions were carried out in a differential flow reactor, at pressures from 0.01 to 1 Torr and temperatures from 500 to 1900 K. It was found that the rates of product formation could be fit by Langmuir–Hinshelwood unimolecular rate expressions, with an accuracy of $\pm 20\%$ under all conditions. Ammonia decomposes to N₂ and the rate of decomposition is fastest on Ir by several orders of magnitude when compared with that on the other metals, becoming flux limited above about 750 K. Ir appears to be the choice catalyst for dehydrogenating ammonia. The heats of adsorption of NH₃ on Pt, Rh and Pd are similar and equal to 16.7, 16.8 and 17.4 kcal/mol, respectively. The apparent activation energy for this reaction is similar on Pt and Rh and equal to 21 kcal/mol, while for Pd and Ir it is 26.2 and 31.2 kcal/mol, respectively.

Keywords: Ammonia decomposition; Palladium; Iridium

1. Introduction

The decompositions of NH₃ on polycrystalline Pt and Rh were described in an earlier paper [1]. It was shown that the rate of reaction on both metals and at all temperatures and pressures could be fit quantitatively with Langmuir–Hinshelwood (LH) unimolecular rate expressions with an accuracy of $\pm 20\%$ under all conditions, over a wide range of temperature and partial pressures. The same conclusion was also reached for the carbon containing small

molecules, HCHO, HCOOH and CH₃OH, as well as for N₂H₄ also on Pt, Rh and Ir [2,3].

The decomposition of ammonia is endothermic:



The Gibbs free energy decreases very rapidly with increasing temperature because the entropy change for this reaction is positive and equal to 28.8 cal/(mol K).

Ammonia is a byproduct of catalytic reactions occurring in the automotive catalytic converter, arising from the reduction of nitric acid with hydrogen, especially under reducing conditions. Ammonia also escapes into the environment during the homogeneous reduction of NO

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with NH_3 injection into the hot gases of internal combustion engines.

For the correlation of data the Langmuir–Hinshelwood model was used. The Langmuir–Hinshelwood (LH) mechanism assumes a single binding state with coverage-independent parameters (a Langmuir isotherm) and that the reaction $\text{A}_g \rightarrow \text{B}_g$ proceeds through the steps:



where ‘s’ indicates an empty surface site and A_s is an adsorbed species A. Eq. (1) is assumed to be an equilibrium step, Eq. (2) the rate controlling step and desorption of product B is assumed to be very fast (negligible adsorption). The rate expression obtained from this sequence of steps is

$$r_A = \frac{k_R K_A P_A}{(1 + K_A P_A)} \quad (4)$$

where k_R , the rate coefficient, is

$$k_R = k_{R0} \exp(-E_R/RT) \quad (5)$$

and K_A , the adsorption equilibrium constant, is

$$K_A = k_a/k_d = K_{A0} \exp(E_A/RT) \quad (6)$$

E_A , E_R , K_{A0} and k_{R0} in Eqs. (5) and (6) are the parameters of the LH model. E_R (kcal/mol) and E_A (kcal/mol) are the reaction apparent activation energy and the apparent heat of adsorption of A, respectively, and k_{R0} (molecules/($\text{cm}^2 \text{ s}$)) and K_{A0} (Torr^{-1}) are the pre-exponential factors for reaction and adsorption, respectively. The reaction pre-exponential k_{R0} , which is related to the frequency of reaction barrier impingement and the adsorption pre-exponential K_{A0} , which is related to the flux to the surface and to the initial sticking coefficient, have been discussed in detail in [1,2].

Measurements were made over a wide range of temperature and reactant pressures so that steady-state surface coverages from zero to sat-

uration are obtained and all parameters in Eqs. (4)–(6) can be measured. Metals must also be free of oxides, nitrides and contaminants and remain clean during reaction conditions to obtain accurate kinetic data and to test the LH mechanism.

The major objective of this study is to examine decompositions of ammonia on Pd and Ir and to compare these reactions with the corresponding ones on Pt and Rh [2] to determine differences between these metals. Also apparent heats of adsorption obtained from the fits of the experimental rates with LH rate expressions are compared with desorption activation energies obtained from desorption of these molecules from noble metal surfaces under UHV conditions.

2. Experimental

Experimental apparatus and procedures were described in more detail in [1,2]. Reactions were carried out in a 400 cm^3 , six-way cross stainless steel reactor. Upstream and downstream valves controlled the flow rate and pumping speed, respectively. Gases were pumped out of the reactor by a mechanical pump with a cold trap to reduce hydrocarbon backstreaming. The base pressure in the reactor was about 10^{-3} Torr. Total reactor pressures between 10^{-3} and 10 Torr were measured with a capacitance manometer, with a precision of ± 0.001 Torr.

Reactor partial pressures of gases were measured by leaking gases into a quadrupole mass spectrometer system to a pressure of 10^{-6} Torr from a base pressure of less than 10^{-8} Torr. They were calibrated against mass spectrometer readings by passing known mixtures of gases through the reactor. Mass spectrometer signals were found to be proportional to partial pressures at all pressures. Cracking of NH_3 on the hot tungsten filament of the mass spectrometer produced about 10% backgrounds of its reaction products.

By measuring the rate of pressure drop from

flasks of known volume, reactant flow rates were determined and reactor residence times ranged from about 0.5 to 10 s. The major advantages of this reactor geometry are an accurately known catalyst area, ease of variation of reactor pressure, flow rate and catalyst temperature and most important, the applicability of the mixed reactor mass balance equation for determining absolute reaction rates:

$$r_i = \frac{F \Delta P_i N_o}{RT_g A_w} \quad (7)$$

In Eq. (7), r_i is the rate per unit area of consumption or formation of species i (in molecules/(cm² s)), F the volumetric flow rate (l/s), ΔP_i the change in partial pressure of species i between reactor and feed conditions (Torr), N_o Avogadro's number, A_w the wire area (cm²), T_g the gas temperature (295 K) and R the ideal gas constant (Torr l/(mol K)).

Because of the large gas diffusivities at these low pressures, reactant concentrations in the reactor are uniform and conversions were maintained below 5% to obtain differential rates, without product inhibition. On Ir, conversions were up to 15% and the partial pressures of ammonia in the reactor were corrected to account for this. Steady states were established within 1–2 s after the wire temperature had attained a desired value. NH₃ (99.9%) was passed through a cold trap at –35°C.

The catalysts, which were resistively heated, were 99.999% purity Pd and Ir wires of 0.025 or 0.0127 cm diameter and lengths from 3 to 15 cm, which corresponds to areas between 0.12 and 1.2 cm². The wires were spot welded to heavy Ni leads and the temperature was measured by Pt–13% Rh thermocouples with an estimated precision of ±2%. Pd was cleaned in O₂ at 0.150 Torr at 1500 K for 3 h when new and for 1 h prior to the experiments. Ir was cleaned in O₂ at 0.150 Torr at 1900 K for the same period as that with Pd. Studies in reactors containing AES [1] have shown that this treatment renders the surfaces free of contaminants.

Several wires of different area were used to obtain the rate data for each gas and 3–4 different wires were used for each reaction to check reproducibility of data. All data were reproducible on each surface and on different samples and over long periods of time to within ±15%.

3. Results

Figs. 1 and 2 show rates of N₂ formation versus surface temperature from the NH₃ decompositions on Pd and Ir. At high temperatures all rates are first order in reactant pressure and all become pressure independent at sufficiently low temperatures, as can be seen in Figs. 1 and 2. Solid curves in all figures are fits to the data with Eq. (4) and the rate expression for each decomposition is indicated in the text.

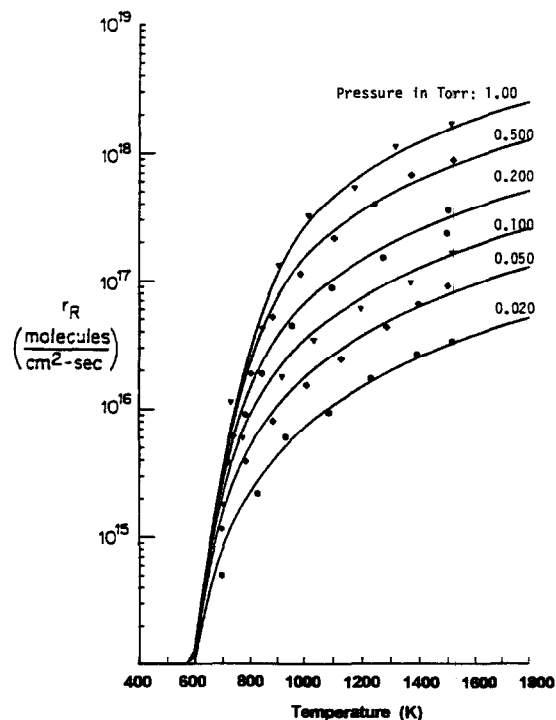


Fig. 1. Rates of N₂ formation from the NH₃ decomposition on Pd versus surface temperature. Partial pressures of NH₃ are as indicated.

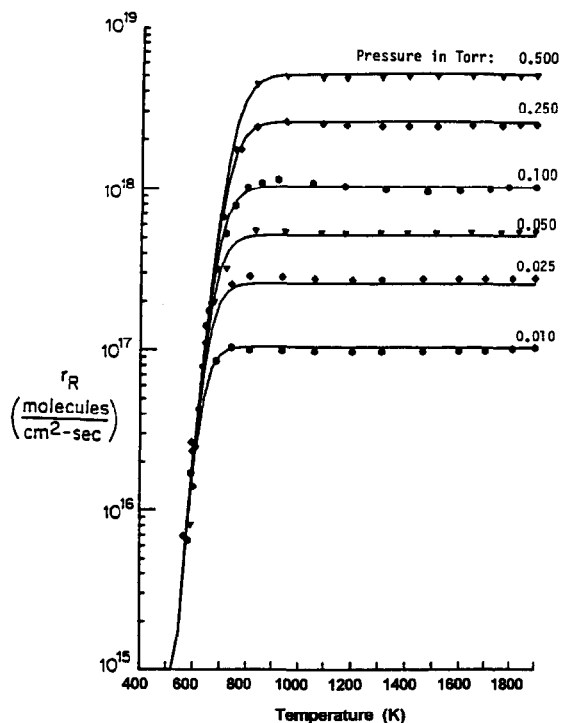


Fig. 2. Rates of N_2 formation from the NH_3 decomposition on Ir versus surface temperature, at NH_3 pressures as indicated.

The values of the rate parameters were independently fitted as in [1–3]. The data (at pressures from 0.01 to 1 Torr and temperatures from 500 to 1900 K) were first fitted with Eq. (4) at low temperatures where $r_{N_2} \rightarrow k_R$ and then once the values of k_{R0} and E_R were determined, the data were fitted at high temperatures where $r_{N_2} \rightarrow k_R K_A P_A$ and the values of E_A and K_{A0} were subsequently fitted [1–3].

3.1. NH_3 on Pd

Fig. 1 shows the rates of N_2 formation from the NH_3 decomposition on Pd. Below 700 K the rates become pressure independent and above 1100 K they are first order with respect to reactant pressure. Below 800 K the NH_3 decomposition is relatively slow on Pd. The reaction probability at 1800 K is 0.005. From the fit of the experimental data the following rate for

the N_2 formation from the NH_3 decomposition was obtained:

$$r_{N_2} = \left\{ 3.1 \times 10^{19} [\exp(-26230/RT)] \right. \\ \left. \times [\exp(17390/RT)] P_{NH_3} \right\} \\ / \left[1 + 5.7 \times 10^{-5} \exp(17390/RT) P_{NH_3} \right] \quad (8)$$

The solid curves in Fig. 1 are drawn from Eq. (8).

3.2. NH_3 on Ir

Fig. 2 shows the rates of N_2 formation from the NH_3 decomposition on Ir. The rate of NH_3 decomposition on Ir is very fast even at low temperatures and varies markedly from those on Pt, Rh and Pd as will be shown in a later section. It becomes flux limited above 750 K with a reaction probability of 0.025. Below 700 K the rate of decomposition becomes pressure independent. This reaction is faster than those of NO and N_2O decomposition at all temperatures.

If a unimolecular reaction is flux limited, then the forward rate in Eq. (1) is comparable to the reaction rate Eq. (2). However, the form of Eq. (4) is still preserved with K_A now being a steady-state parameter rather than the adsorption equilibrium constant. In the high temperature limit the rate becomes $r_R = k_a P_A$ if $k_R \gg k_d$. Since $k_a = S_o / (2\pi MRT_g)^{1/2}$, r_R should be nearly independent of surface temperature. With the assumption that $k_R \gg k_d$ the form of Eq. (4) becomes:

$$r_R = \frac{k_a P_A}{1 + (k_a/k_R) P_A} \quad (9)$$

The following rate expression was obtained for the rate of N_2 formation from the NH_3 decomposition on Ir:

$$r_{N_2} = \frac{1.05 \times 10^{19} P_{NH_3}}{(1 + 1.2 \times 10^{-9} \exp(31200/RT) P_{NH_3})} \quad (10)$$

4. Catalyst morphology

The surface morphology of Pd and Ir wires was found to change during reaction. After heating in O₂ and in oxygen containing gases for 3–4 h and above 1300 K, surfaces were observed to develop a dull appearance. Similar changes had also, been observed on Rh, but not on Pt [1]. SEM photographs showed that these pyramidal protrusions grow on single crystal planes along grain boundaries. Their size and shapes are about the same as those observed on Rh. Protrusions, however, grew to a smaller extent on Pd and to a much smaller extent on Ir when compared with those that grew on Rh.

This change in the morphology of the Pd and Ir wires appears to affect reaction kinetics only as an area change, since neither the activation energies nor the heats of adsorption appeared to be altered. The only affect of this surface activation was to increase all rates by about a factor of 1.2–1.4. This was ascertained by making complete runs of the rate versus temperature at low pressures, then activating the wires, repeating the runs and comparing rates. The geometrical area change (surface area of a pyramid/base area) was estimated from SEM pictures to be about 1.5, consistent with the rate changes. All rates reported here were taken on activated Pd and Ir wires, but rates are reported on the basis of the initial wire area.

NH₃ was also found to attack Pd and form

holes. Under reducing conditions holes of average diameter ranging from 0.2 μm up to 0.8 μm were formed on Pd upon exposure to NH₃. This change occurred gradually and affects the rates only as an area change, apparently not affecting kinetic parameters. This change was even more dramatic upon exposure of the Pd catalysts to hydrazine (N₂H₄).

5. Discussion

5.1. Reaction parameters

The quantitative agreement of all rates with LH rate expressions (solid curves in Figs. 1 and 2), as was the case with these decomposition reactions on Pt and Rh (2), shows that this is an excellent model to fit unimolecular reaction rates and it suggests that the mechanism implied (adsorption–desorption equilibrium and coverage independent parameters) is a reasonable description of these processes. Therefore the quantities in k_R should be related to barrier crossing events and those in K_A to adsorption and desorption of species A. The LH rate parameters on Pt and Rh have been discussed in detail in [1,2]. Here, in Table 1, these parameters are compared on all four metals.

The heats of adsorption of NH₃ on the three metals Pt, Rh and Pd are similar. Under UHV conditions in TPD experiments [4–6] NH₃ on Pt

Table 1
Comparison of the rate parameters on Pt, Rh, Pd and Ir for the NH₃ decomposition

	Pt	Rh	Pd	Ir
k_{R_0}	1.0×10^{23} ($\pm 0.2 \times 10^{23}$)	2.9×10^{23} ($\pm 0.5 \times 10^{23}$)	5.4×10^{23} ($\pm 0.9 \times 10^{23}$)	8.8×10^{27} ($\pm 1.1 \times 10^{27}$)
K_{A_0}	4.4×10^{-5} ($\pm 0.6 \times 10^{-5}$)	3.1×10^{-5} ($\pm 0.4 \times 10^{-5}$)	5.7×10^{-5} ($\pm 0.8 \times 10^{-5}$)	—
E_R	20.9 (± 1.1)	21 (± 1.1)	26.2 (± 1.3)	31.2 (± 1.8)
E_A	16.7 (± 0.9)	16.8 (± 0.9)	17.4 (± 0.9)	—

k_{R_0} : molecules/(cm² s), K_{A_0} : Torr⁻¹.
 E_A , E_R : kcal/mol.

is fairly unreactive with all of the NH_3 desorbing without dissociation, although some dissociation occurs above 600 K. The desorption activation energy for NH_3 on Pt group metals has been reported to be 8.6 kcal/mol [4,6] for the weakly bound state and between 16 and 23 kcal/mol [7] for the more strongly bound states. The values of the heat of adsorption of NH_3 of 16.7, 16.8 and 17.4 kcal/mol during the NH_3 decomposition on Pt, Rh and Pd, respectively, agree well with the reported desorption activation energies.

The activation energies for the decomposition of NH_3 on Pt and Rh are the same, and it is highest on Ir. The reaction activation energy for the NH_3 decomposition on Rh (100), (110) and (111) is reported to be 19 kcal/mol [8], and the value of 21 kcal/mol on polycrystalline Rh is in good agreement.

5.2. Comparison between metals

Fig. 3 shows the rate of NH_3 decomposition on Pt, Rh, Pd and Ir. NH_3 decomposes very fast on Ir, becoming flux limited, depending on pressure, above 700–800 K. Decomposition of NH_3 on Pt and Rh is similar at all temperatures, varying only by a factor of two and this is due to the Rh wires being activated. On Pd the NH_3 decomposition is very slow below about 1000 K and at low temperatures it is slower by a factor of 10 from the corresponding decomposition reactions on Pt and Rh, while at high temperatures the NH_3 decomposition reaction on Pt, Rh and Pd is similar. At low temperatures it is faster on Ir by up to three orders of magnitude when compared with the other metals.

It is interesting to speculate on the possible mechanism leading to NH_3 dissociation. On Pt-group metals N_2 apparently does not adsorb, so recombination of adsorbed N species and desorption of nitrogen should occur very rapidly. Decomposition of NH_3 should most likely proceed through successive dehydrogenation reactions of adsorbed NH_x species [9]. Ammonia adsorbs through the lone pair of electrons on the

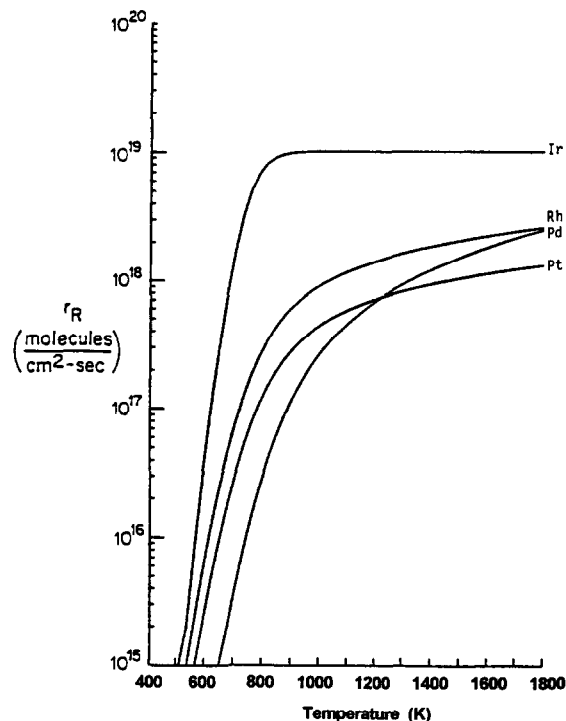


Fig. 3. Comparison of the rates of N_2 formation from the NH_3 decomposition on Pt, Rh, Pd and Ir, at a partial pressure of NH_3 equal to 1.00 Torr.

N atom and once it dissociates, continued dissociation and recombination of N and H atoms to N_2 and H_2 should be the only energetically favored processes.

Ammonia decomposition has been studied extensively on catalysts other than the noble metals. Tamaru [10] discusses ammonia decomposition in terms of LH kinetics with one overall rate determining step. On Fe, in Temkin–Pyzhev kinetics, N_2 desorption is slow and is the overall rate determining step [10]. Norskov and Stolze studied the ammonia synthesis reaction on Fe and from ultrahigh vacuum–single crystal results extrapolated to predict the performance of industrial ammonia synthesis catalyst [11–14]. In the aforementioned study the rate determining step was assumed to be the formation of atomic chemisorbed nitrogen species from a molecular precursor state. Dumesic and Trevino [15] also report that the dissociation of

a molecular dinitrogen precursor species is a slow step in the mechanism in the ammonia synthesis reaction on Fe.

It is also interesting to compare the rate of decomposition of NH_3 with that of N_2H_4 reported earlier [2,3]. The decomposition rate of hydrazine at high temperatures on Ir is faster than that of NH_3 on Ir by about a factor of 4 and this may be partly due to differences in the sticking coefficients of the two molecules. At low temperatures N_2H_4 decomposition on Ir is much faster when compared to NH_3 decomposition on Ir by up to two orders of magnitude. Also the rate of decomposition of hydrazine is almost identical on Pt, Rh and Ir, but the rate of NH_3 decomposition varies remarkably on Ir when compared to the other three metals namely Pt, Rh and Pd.

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