CATALYTIC EFFECTS IN THE VARIOUS STAGES OF
PLASMA SYNTHESIS OF AMMONIA

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ABSTRACT

The plasma synthesis of ammonia was studied in the presence of some transition metals. At low pressures and intermediate temperatures Pt sputtered on the walls of a glow discharge increased the NH₃ yield. The "catalytic" effect could be enhanced by the presence of the same metals in the spatial afterglow and the cold trap where NH₃ is mostly formed.

1. INTRODUCTION

Often in plasma synthesis the overall process is attributed to plasma reactions. It is, however, the result of a number of steps occurring in sequential stages which begin in the plasma and depend on the configuration of the reactor for successful termination (1). The absence of a spatial afterglow region and/or cold trap results in low reactor yields and/or the unsuccessful synthesis of a number of compounds (2-5).

The role of heterogeneous processes in plasma synthesis became evident when product concentration was found to depend on the surface-to-volume ratio of the reactor (6,7). Subsequently, it was found that foreign substances in the solid phase, which are called "catalysts", shift the steady-state concentrations of the products in several plasma reactions (8). The effect is unique to the field of plasma chemistry and has found application for increasing the reactor yield in plasma synthesis (9). For delineating the degree of such catalytic activity in the different stages of plasma synthesis we have studied the formation of NH₃ from N₂ and H₂ with materials (mostly transition metals) located in the plasma, in the spatial afterglow, and/or in the cold trap.

2. EXPERIMENTAL

A conventional discharge-flow system constructed of 15 mm o.d. Pyrex tubing was used (Fig. 1). At one end of the tubing a gas inlet system consisting of metering valves (V₁, V₂), rotameters (R₁, R₂), and a manometer (M) allowed the controlled flow of commercial quality N₂ and H₂ at desired pressures; at the other end a U-trap (T) in series with an inlet-tube trap pumped via
a throttling valve $V_3$ was used for condensing NH$_3$ at 77 K. Mixtures of N$_2$ and H$_2$ were excited using (a) air-cooled 1/4 Evenson cavity C tuned to 2.45 GHz microwaves supplied from a Scintillonics Model HV 15A generator and/or (b) electrodes $E_1$, $E_2$ of 1x1 cm made from 0.25 mm thick metal foils connected by glass-sleeved tungsten wires to a 15 kV transformer operated by 50 Hz current. The design of the apparatus allowed the introduction of catalysts into various zones (P/A, A/C), each of which could be maintained at a desired temperature during the course of a run.

The amount of ammonia collected in a given run was calculated from the pressure read on an absolute pressure gauge (G) located in a calibrated volume of the apparatus at room temperature. The reaction time was calculated from the reaction volume and the flow rate under the experimental conditions.

3. RESULTS AND DISCUSSION

a) The non-catalyzed reaction was studied (10) using 2.45 GHz microwave excitation to avoid contamination by electrode materials. In the power range of 5-10 W cm$^{-2}$ and a total pressure less than 1 torr [$p$(N$_2$) = 0.7 torr, $p$(H$_2$) = 0.2 torr] the conversion of nitrogen to NH$_3$ was nearly 2% for gas flow rates in the range 10-100 cm$^3$/s.

b) About the same conversion was obtained (11) using Al electrodes in a discharge at 15 mA and a total pressure less than 10 torr [$p$(N$_2$) = 2 torr, $p$(H$_2$) = 5 torr]. When Pt electrodes

![Fig. 1. Schematic of the apparatus.](image-url)
were used the conversion quadrupled to approx. 8%, the activity for other electrode materials varied in the following order: Pt > Ag > Fe > Cu > Al.

c) With Pt sputtered onto the glass walls (49 cm²) of the plasma volume (16 cm³) in a discharge using Al electrodes (region marked P/A in Fig. 1) at 16 mA, and a total pressure less than 1 torr (as in a) above), [NH₃] increased with reaction time and attained a value of 65 mol% for H₂/N₂ = 1.7 at 640 K, corresponding to 33% N₂ conversion (Fig. 2). Nitrogen conversions as high as 50 mol% were observed for H₂/N₂ = 2.2 at 830 K, but [NH₃] was 44% only. For longer residence times, [NH₃] exhibited a maximum as the temperature and/or H₂/N₂ ratio was increased. For nearly the same reaction time (approx. 1.5s) doubling the H₂/N₂ ratio increased [NH₃] six-fold at 400 K and three-fold at 450°K; for nearly the same H₂/N₂ ratio (0.9) doubling reaction time decreased [NH₃] significantly. Figure 3 shows that the pressure variation of [NH₃] and NH₃/N₂ are nearly exponential (correlation coefficients 0.990-0.996²) for the three different flow rates studied. At the higher pressures the conversion of nitrogen increased, but [NH₃] decreased with reaction time, presumably due to hydrazine formation.
Fig. 3. Variation of \( \text{NH}_3/\text{N}_2 \) and [\( \text{NH}_3 \)] (inset) with pressure for three flow rates (mL/min): 1. \( \text{N}_2/\text{H}_2 = 78/110 \); 2. \( \text{N}_2/\text{H}_2 = 80/125 \); 3. \( \text{N}_2/\text{H}_2 = 100/135 \). Dots represent values calculated based on a least squares fit of the data using equation \( \log(Y) = mX + B \).

d) With Pt sputtered onto the glass walls (49 cm\(^2\)) of the spatial afterglow region (P/A in Fig. 1) of a microwave cavity discharge (experimental conditions as in a) above) the highest concentration of \( \text{NH}_3 \) was found to be 27 mol\% for \( \text{H}_2/\text{N}_2 = 5.3 \) at 630 K (10). When \( \text{N}_2 \) previously dissociated in a microwave cavity was mixed with \( \text{H}_2 \) and passed over Pt under the same experimental conditions, the same concentration of \( \text{NH}_3 \) (27\%) was obtained. Since Pt chemisorbs N readily, and \( \text{H}_2 \) by a dissociative mechanism, formation of NH is to be expected: \( \text{N}(\text{ads}) + \text{H}_2 \rightarrow \text{NH} + \text{H} \). The NH radical has been detected spectroscopically in significant amounts near the electrode regions in 50 Hz discharges (3). Because excess \( \text{H}_2 \) appears to favor the cold trap formation of \( \text{NH}_3 \) (Fig. 2), the energetically-favored reaction \( \text{NH} + \text{H}_2 = \text{NH}_2 \) must be occurring in the synthesis, with the \( \text{NH}_3 \) yield limited by the formation of NH rather than H-atom recombination.

e) Figure 4 presents data on \( \text{NH}_3 \) formation when different metals were placed in the spatial afterglow (A/C in Fig. 1) at relatively low temperatures (77-380 K) under the same experimental
conditions as in b) above. Again, Pt gave the highest yield of ammonia at all the temperatures studied. The yields normalized for unit surface area followed the order Pt > Pb > Ni > Ag > Cu > Zn, which does not correlate with the electron work function or % d-character of the metals. The increasing NH$_3$ yield with decreasing temperature of the afterglow region is additional verification of the previously reported (3,4) finding that NH$_3$ is formed essentially in a cold trap.

f) Figure 5 shows the dependence of ammonia formation on metals placed in the inlet-tube trap when the plasma was formed using stoichiometric ratios of N$_2$ and H$_2$ in a discharge tube (P/A in Fig. 1) with and without Pt sputtered on the walls. More NH$_3$ was formed when Pt and Ag were placed in the cold trap, the increase being greater at lower pressures which favor surface reactions and shorter residence times which reduce the loss of ammonia precursors. At the higher pressures some hydrazine was deposited on the walls of the tube near the exit of the plasma zone.

In summary, a plasma chemical system should be designed with provision for a catalyst, such as Pt sputtered on the walls and maintained at desired temperatures, in all the three regions of activity to achieve high product yields.
Fig. 5. Dependence of ammonia formation on metals placed in a cold trap at 77 K. The closed points are for the Pt sputtered discharge tube at 670 K; open points for a clean discharge tube for which the variation of wall temperature with pressure at constant current is shown in the inset.

REFERENCES