EFFECT OF A PLATINUM CATALYST IN THE SPATIAL AFTERGLOW ON THE PLASMA SYNTHESIS OF AMMONIA

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ABSTRACT

Formation of ammonia by the reactions of (1) N_2 and H_2 subjected to a microwave-sustained plasma and (2) N_2 predissociated in a microwave plasma and then mixed with H_2 was studied in the presence of a Pt catalyst in the spatial afterglow. The catalytic effects in the afterglow were significantly greater than those reported for the glow itself.

1. INTRODUCTION

Heterogeneous catalysis in a plasma has been studied in some detail (1). In some studies (2,3) catalysts such as Mo, MoO_3 and WO_3 were kept immersed in the plasma; in some others catalysts such as Ni and Pt were coated (4) on the discharge tube or introduced (5,6) directly into the interelectrode space. It was found that the combined effects of catalysts and an electrical discharge produced stationary concentrations of reaction products exceeding the stationary concentrations in the plasma without the catalysts.

In some plasma systems, notably H_2+O_2 (7,8) and N_2+H_2 (9) the yields of products depend on the reaction time of the dissociated gases in the spatial afterglow rather than in the plasma itself. It was, therefore, desirable to investigate heterogeneous catalysis in the spatial afterglow. A Pt catalyst and the ammonia synthesis were chosen for this study in view of the known effects on the heterogeneous catalysis in the plasma (4,5) and on the product yield in the spatial afterglow (9), respectively. The use of a microwave discharge allowed a comparison of the catalyzed reaction with the non-catalyzed reaction.

2. EXPERIMENTAL

The apparatus is shown in Fig. 1. The gas inlet system consisted of a set of rotameters (R1,R2) and metering valves (V1, V2), which allowed the controlled flow of commercial quality N_2 and H_2 at pressures indicated by the oil manometer M and/or a General Electric thermistor gage T. Air-cooled λ/4 Evenson cavities (C1-C3) were used to study the non-catalyzed (C1) and catalyzed (C2) N_2+H_2 reactions and the catalyzed (C3) $N+H_2$ reaction. The catalyst consisted of a spiral of Pt wire inside the Pyrex tubing which was heated by a tubular furnace F. A 60 Hz glow discharge between Al electrodes E1 and E2 deposited some of the Pt on the glass walls. The ammonia was condensed at 77 K in the first U-trap which was cooled by liquid nitrogen. At the end of a run, usually of 1 hr duration, the ammonia was distilled into the second U-trap and its pressure in the calibrated volume V measured at room temperature using the absolute pressure gage P. Pressure in the system was controlled by the throttling valve V3 through which the apparatus was pumped by a two-stage diffusion pump. The plasma was produced by a Tesla-coil and sustained in the appropriate cavity by tuning it to 2.45 GHz microwaves supplied from a Scintillonics Model HV 15A generator. The absorbed power was taken to be the difference between the applied and reflected powers and was varied in the range of 5-10 W cm^{-3} at gas pressures <1 torr and flow rates up to 100 cm^3 s^{-1}.

3. RESULTS AND DISCUSSION

Figures 2 and 3 show the % conversion of N_2 to NH_3 as a function of the residence time of N_2 in the spatial afterglow. The residence time was caculated (7) from the reaction volume and the flow rate under the experimental conditions. With N_2+H_2 mixtures containing less than stoichiometric amounts of H_2 the maximum observed conversion of N_2 was less than 2% in the non-catalyzed reaction, but greater than 12% in the catalyzed reaction at 300 K. The contact time with the catalyst (0.2-2.8 s) was about one-fourth the residence time of the gases (0.8-10.8 s) in the afterglow. With more than stoichiometric amounts of H_2 the maximum observed conversion of N_2 was about 50%. Doubling the catalyst temperature increased the conversions, the maximum observed conversions of N_2 being greater than 80%. When N_2 previously dissociated in a microwave cavity was mixed with H_2 and passed over the same catalyst, the conversions decreased by 50% at 300 K and 20% at 633 K. At lower pressures and higher flow rates of N_2 the residence times could be decreased and the conversions of N_2 increased, but the temperature effect was not very significant. In all cases the % reaction increased linearly with contact time of the catalyst and gases from the plasma.

Increasing the pressure and/or concentration of N_2 in the gas mixture increased the % yield of NH_3. A mixture containing 12 mole% N_2 at 0.1 torr yielded up to 13 mole% NH_3. As the pressure was increased to 0.7 torr the NH_3 yield increased to about 27 mole% (Table 1). This is very much greater than the best value (12%) reported by Eremin et al (5) for heterogeneous catalysis by Pt in a glow discharge. The NH_3 yield decreased when N_2 was predissociated and mixed with H_2, but the decrease was not very significant in the experiments at the relatively higher pressure (0.7 torr) and temperature (633 K).

Since a glow discharge in N_2+H_2 mixtures or ammonia results in excited molecules as well as atoms (1,6,10) NH was initially formed on the catalyst surface probably by the reaction

$$N_2^* + H \rightarrow N + NH \qquad [1]$$

The excited state is possibly the triplet $A^3\Sigma_u^+$ which has an energy of ≈6 eV. This state has only an intercombination transition and is therefore metastable (5). In the predissociation experiments the following reactions may have exclusively produced radical intermediates such as NH and NH_2:

$$N + H_2 \rightarrow NH + H \qquad [2]$$

$$N + H_2 \rightarrow NH_2 \qquad [3]$$

Ammonia is formed by reactions such as

$$NH + H_2 \rightarrow NH_3^* \qquad [4]$$

$$NH_2 + H_2 \rightarrow NH_3 + H \qquad [5]$$

The NH_3^* molecules formed by reaction [4] have excess energy which must be removed for their stabilization. The energy can be removed by efficient quenching (6). But the low conversions in experiments without a catalyst suggested that the energy removal is more effective on the metallic surface of the catalyst or that only the ammonia precursors such as NH and NH_2 were formed and stabilized on the catalyst surface and that the precursors then reacted to form ammonia in a sufficiently cold trap (6). Further, the higher yield of NH_3 when N_2+H_2 was subjected to the plasma indicated that reaction [1] was preponderant in this system. The temperature effect when excess N_2 (and not H_2) was present probably arose from the occurrence of increased adsorption of atomic nitrogen and excited nitrogen molecules on the catalyst surface prior to formation of the radical intermediates:

$$N_2^*(ads) + H \rightarrow NH(ads) + N \qquad [6]$$

$$N(ads) + H_2 \rightarrow NH_2(ads) \qquad [7]$$

The role of the metal surface can also lead to an increase in the recombination of H atoms and to their low concentration in the gas phase. As a result, the rate of decomposition of ammonia by the reaction

$$NH_3 + H \rightarrow NH_2 + H_2 \qquad [8]$$

is significantly reduced. Thus, in the presence of the Pt catalyst in the N_2+H_2 system not only is the formation of NH_3 increased but its decomposition inhibited. Application of the specific energy method (1,5) showed an increase of the rate constant (k_f) for the formation of ammonia and a decrease of the constant (k_d) for its decomposition (Table 2). An increase in k_f when both N_2 and H_2 were subjected to the plasma rather than N_2 alone is consistent with the mechanism discussed.

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TABLE 1. PERCENT YIELD OF AMMONIA

Reaction	N_2 mole%	$p(N_2)$ torr	$p(H_2)$ torr	Catalyst (Pt) temp., K	NH_3 mole%
$N_2 + H_2$	50-86	0.7	0.2	non-catalyzed	1-2
	62			300	8
				633	14
	16			300	19
				633	27
	34	0.1	0.4	300	6
				633	8
	12			300	12
				633	13
$N + H_2$	62	0.7	0.2	300	3
				633	13
	16			300	10
				633	26
	34	0.1	0.4	300	2
				633	2
	12			300	4
				633	3

TABLE 2. RATE CONSTANTS FOR THE FORMATION (k_f) AND DECOMPOSITION (k_d) OF AMMONIA

Reaction	$p(N_2)$ torr	Catalyst (Pt) temp., K	Liter W^{-1} h^{-1}	
			k_f	k_d
$N_2 + H_2$	0.7	non-catalyzed	0.04	0.035
		300	0.18	0.012
		633	0.30	0.014
	0.1	300-633	0.08	0.005
$N + H_2$	0.7	300	0.085	—
		633	0.23	—
	0.1	300-633	0.02	0.006

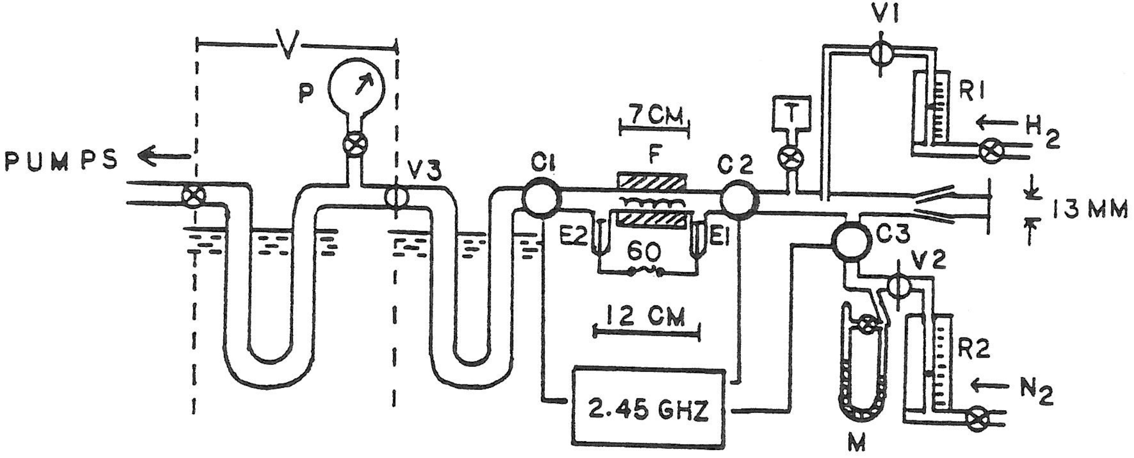

Fig. 1. Apparatus for the synthesis of ammonia in presence of catalysts in the spatial afterglow.

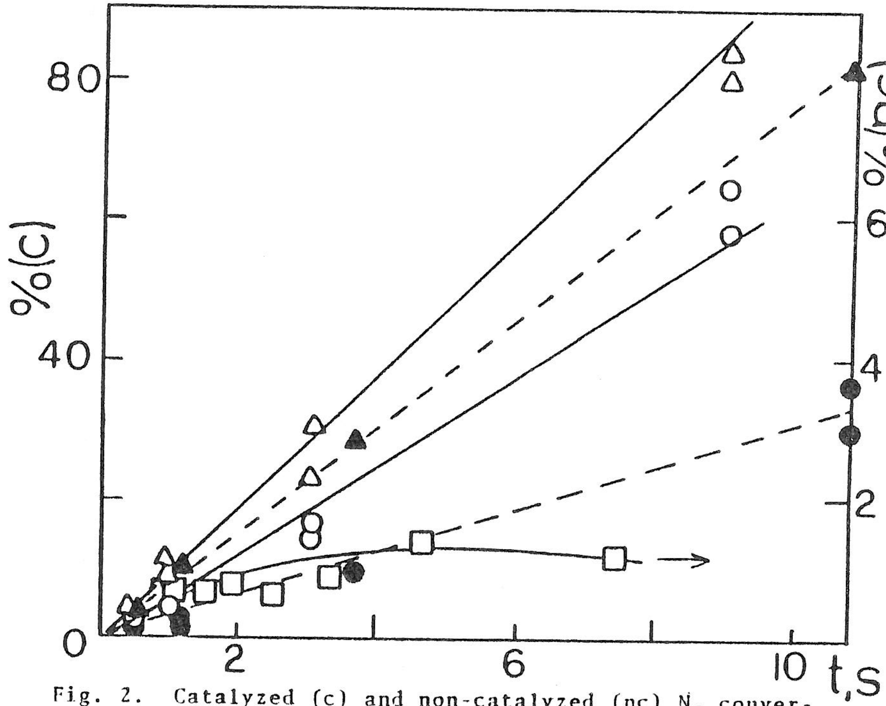

Fig. 2. Catalyzed (c) and non-catalyzed (nc) N_2 conversion to NH_3 *vs* reaction time (t) in the spatial afterglow of $N_2 + H_2$ (–) and $N + H_2$ (--) at 0.7 torr N_2 and 0.2 torr H_2.

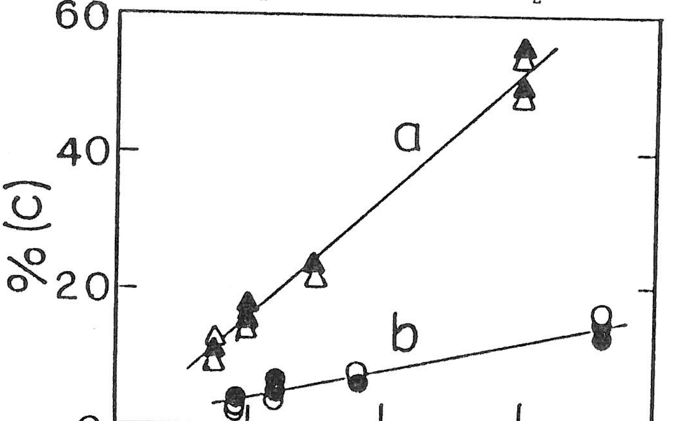

Fig. 3. Catalyzed (c) N_2 conversion to NH_3 *vs* reaction time (t) in the spatial afterglow of (a) N_2+H_2 discharge and (b) $N+H_2$ at 0.1 torr N_2 and 0.4 torr H_2. (Open and closed points for 300 and 633 K, respectively.)