

Ammonia Synthesis by Means of Plasma over MgO Catalyst

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Ammonia synthesis from H₂-N₂ mixed gas was studied at room temperature in a glow-discharge plasma in the presence of metals or metal oxides. Magnesia (MgO) and calcia (CaO), which are oxides with solid basicity, revealed catalytic activity in the plasma synthesis of ammonia, although they are catalytically inactive in industrial ammonia synthesis. The acidic oxides (Al₂O₃, WO₃, and SiO₂-Al₂O₃) lead to the consumption of the reactant, i.e., the H₂-N₂ mixed gas. No ammonia was isolated. Metal catalysts showed higher activity than the above basic oxides. They have, however, different activities. The reaction was faster over the active materials than over sodium chloride (NaCl) or glass wool or in a blank reactor without any catalyst.

KEY WORDS: Ammonia synthesis; catalysis in plasma; MgO; CaO; Al₂O₃; WO₃; metal catalysts.

1. INTRODUCTION

Ammonia (NH₃) is industrially synthesized under high pressure and temperature (e.g., 400°C and 200 atm). A catalyst is necessary to make the reaction faster. Iron (Fe) is known to be the best catalyst and is widely used. Osmium (Os) and ruthenium (Ru) have also high catalytic activity. The transition metals of the first period (Ti through Ni) are also catalytically active. They cannot be compared with iron in activity and in economy. A small addition of promoters makes the activity of the iron catalyst higher. They are alkali metals or alkaline earths, and such oxides as MgO, CaO,

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Al_2O_3 , and SiO_2 . The promoter alone does not exhibit catalytic activity at all.

It has long been known that ammonia can be produced in a glow discharge plasma⁽¹⁻¹⁴⁾ in which the electron temperature is higher than the ion temperature. Recently, attention has been paid to synthesis using plasmas, since other products can be expected to be produced than are known in thermal reactions. One example is a diamond film,⁽¹⁵⁻²⁴⁾ since thermodynamics tells us that diamond is formed under high pressure and temperature. Another example is ammonia synthesis in a plasma and solid catalyst.⁽²⁵⁾ The reaction with a catalyst proceeds faster than when the plasma is in contact with a passive solid surface (e.g., glass). The fraction of ammonia in the reacting gases is larger than that calculated from thermodynamics. This report is concerned with the acceleration of the rate of ammonia production using a plasma with a catalyst.

2. EXPERIMENT

2.1. Apparatus

Figure 1 illustrates the circulating system for the reaction with a total volume of 160 cm^3 . It is composed of a reactor, a gas trap, a liquid nitrogen

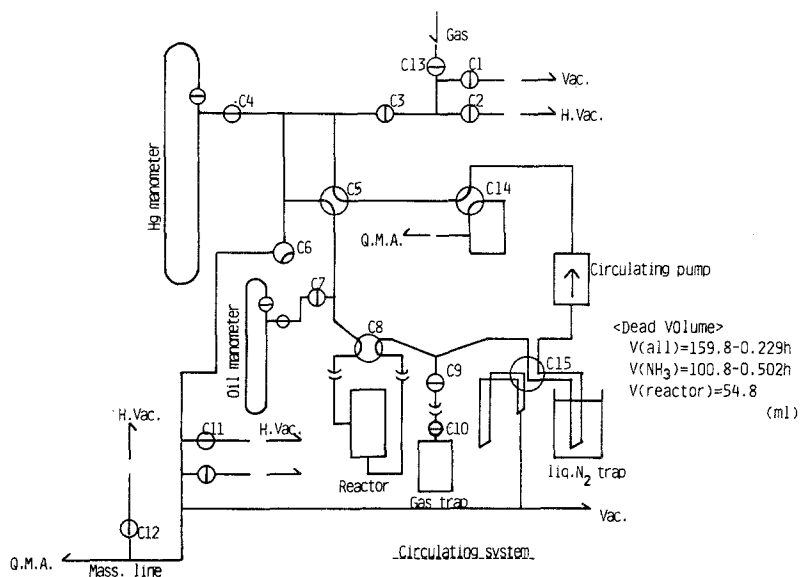


Fig. 1. Apparatus for the plasma synthesis of ammonia.

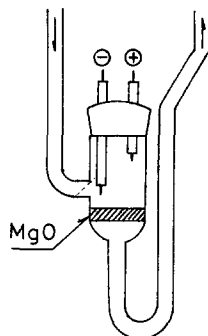


Fig. 2. Reactor for ammonia synthesis.

trap, vacuum lines, a circulating pump, manometers, and a QMA (quadrupole mass analyzer).

Figure 2 shows the Pyrex-glass reactor which is equipped with a pair of tungsten electrodes at the head. A catalyst is mounted on glass wool which is filled at the bottom of the reaction vessel. The distance between the catalyst and the cathode is 3 mm.

2.2. Preparation of Catalysts

The catalysts were prepared as follows:

1. MgO(A): Magnesium hydroxide $\text{Mg}(\text{OH})_2$ (Wakoh Chem. Co. Ltd.) was washed twice with a large amount of pure water, dried, and calcined in air at 700°C for 3 h. MgO thus prepared was shaped into a thin disk which was then crushed.
2. MgO(B): Magnesium oxalate $\text{Mg}(\text{COO})_2$ (Wakoh Chem. Co. Ltd.) was decomposed under evacuation at 700°C for 16h.
3. CaO: quicklime (Wakoh Chem. Co. Ltd.) was used without purification.
4. Al_2O_3 : Neobead GB (Mizusawa Chem. Co. Ltd.) was used.
5. WO_3 : WO_3 gel was precipitated from a sodium tungstate solution with hydrochloric acid.
6. NaCl: A special grade of NaCl (Wakoh Chem. Co. Ltd.) was used.
7. $\text{SiO}_2\text{-Al}_2\text{O}_3$: A $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst manufactured by Shokubai Kagaku Co. Ltd. was used. The ratio of SiO_2 to Al_2O_3 was 87:13.

The particle size of the catalysts was made uniform with a sieve of 20–60 mesh. The amount of catalyst was 0.8 g for a batch. The surface area of the catalyst was, for example, $31.3 \text{ m}^2/\text{g}$ for MgO(A) and $165 \text{ m}^2/\text{g}$ for MgO(B).

In advance of each experiment the catalyst was loaded into the reactor, which was then evacuated at 400°C for 1 h. NaCl and glass wool were evacuated at room temperature for 1 h.

2.3. Experimental Procedure and Analysis of the Reaction

A mixed gas of H₂ and N₂ (ratio 3:1) was introduced into the system at a pressure of 10 Torr. A high DC electric voltage was applied to generate a plasma. The discharge current was kept constant at 6 mA. The reaction was performed at room temperature. The reacted gas was quenched in a liquid-nitrogen trap. Progress of the reaction was observed from the total pressure decrease which was measured with a manometer every 5 min for half an hour. Measurement was stopped before half an hour in the case where the pressure decreased so rapidly that the discharge became unstable. Reaction products were analyzed with the QMA. A volumetric analysis of ammonia verified the values obtained by the QMA. Both adsorbed and absorbed species in the catalyst were analyzed by means of temperature programmed desorption (TPD) with the help of QMA. The temperature was raised at the rate of 20°C/min.

The MgO used catalyst was characterized with ESCA. The sample was shaped into a disk of 1 cm in diameter and 1 mm thick.

The material balance (M.B.) is defined as

$$\text{M.B.(\%)} = \frac{2 \cdot [\text{NH}_3]}{[\text{RED}]} \times 100 \quad (1)$$

The amount of ammonia [NH₃] was measured by a volumetric method. The denominator [RED] implies the amount of reactants consumed during the reaction. The quantity was measured by a volume decrease.

3. RESULTS

3.1. Reaction without a Catalyst

Figure 3 shows the total pressure decrease (Δp) due to ammonia formation. The pressure decreased linearly with time t :

$$\Delta p = -kit, \quad (2)$$

where i is the electric current and k is a constant which depends on experimental conditions, e.g., the shape of the reactor and the mixing ratio of the reacting gases. Brewer⁽²⁾ studied the factors that influence the constant k . He found no influence of the pressure and temperature of the reacting gases, and of an electric field applied from outside, on the constant k .

Differentiation of Eq. (2) with respect to time gives the rate v_{NH_3} of the ammonia formation:

$$v_{\text{NH}_3} = -d\Delta p/dt = ki \quad (3)$$

This is the slope of the linear line in Fig. 3. The values of v_{NH_3} at 6, 7, and 8 mA are 0.092, 0.11, and 0.13 Torr/min, respectively. Since v_{NH_3} is proportional to current, as is seen from Eq. (3), the rate per unit current, dv_{NH_3}/di , is the constant k . The value in our system is 20.4 (Torr/min)/A. Brewer obtained the values with a double U tube as 20.8,⁽¹⁾ with a single U tube as 11.7,⁽¹⁾ and with an arc discharge as 3.14 (Torr/min)/A.⁽³⁾

The current efficiency η is defined as the number of ammonia molecules (n_{NH_3}) produced by the number of electrons q passed through the reactor:

$$\eta = n_{\text{NH}_3}/q \quad (4)$$

This is equivalent to the above constant, since η can be calculated from k . Ammonia is converted by the relation

$$n_{\text{NH}_3} = \Delta p(V/RT) \quad (5)$$

where R is the gas constant, and V and T refer to volume and temperature of the gas, respectively. In our device, V is 160 ml, T is 300 K, and i is 6 mA. The quantity η is expected to be 28% from the current flow. However, we obtained 8.94 μmol of NH_3 after half an hour. The actual value of η was obtained from Eq. (4):

$$\eta = 8.94 \times 10^{-6} / 1.12 \times 10^{-4} \times 100 = 8\%$$

Twenty-five electrons are necessary to form two molecules of ammonia. The observed value, was 1/3.5 of the expected value. Brewer obtained a far better efficiency of 3.65 ammonia molecules per electron.⁽¹⁾

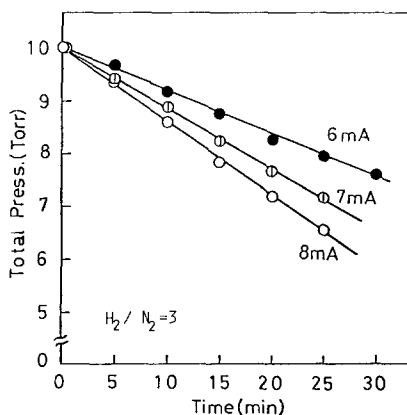


Fig. 3. Total pressure decrease due to the reaction without a catalyst.

3.2. Reaction over Inactive Substances (Glass Wool and NaCl)

Figure 4 compares the pressure decrease over glass wool and NaCl with that of a blank. The values of the material balance were all close to one, indicating that almost all the ammonia was collected.

The filled circles stand for the amount of ammonia produced in the reaction (cf. right ordinate). Use of the glass wool and NaCl yielded $10 \mu\text{mol}$ of ammonia. In the blank case the yield was $8 \mu\text{mol}$. There is no significant difference among them. Therefore, glass wool and NaCl did not act as a catalyst. The loading of a substance did not affect the flow rate of the gas.

One can expect the "wall effect," which implies the acceleration of a reaction by the contact of a plasma with a cold wall.⁽²⁶⁾ Difference of the ammonia yield between a blank and an inactive substance might be ascribed to this effect. Our difference is, however, so small that we can neglect the wall effect.

3.3. Reaction over Basic Catalyst (MgO and CaO)

The total pressure did not decrease linearly with time when a basic catalyst was used (Fig. 5). The reaction rate with MgO(A) was 2–3 times faster than that of a blank. Thus, magnesia acts as a catalyst of the ammonia synthesis with a plasma. The pressure drop with MgO(B) was faster than that with MgO(A). The rate with MgO(B) was, however, not as fast as could be expected from its large surface area.

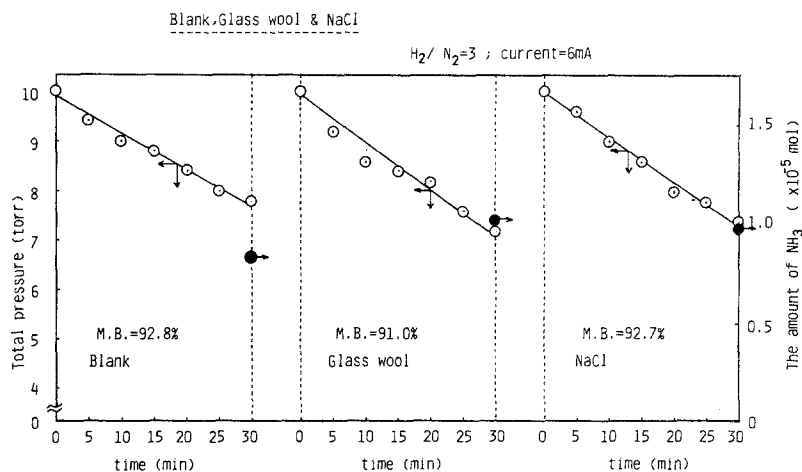


Fig. 4. Total pressure decrease with time. Sodium chloride and glass wool show no catalytic activity. The filled circles denote the amount of ammonia produced in half an hour (cf. the right ordinate).

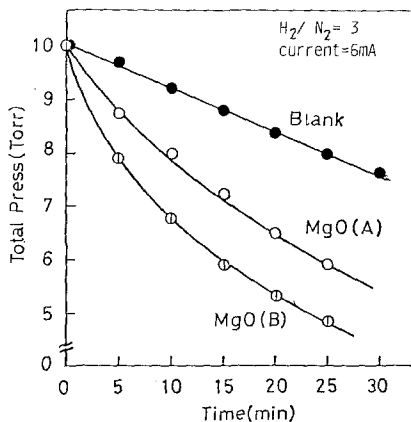


Fig. 5. Total pressure decrease with respect to time in the presence of a MgO catalyst.

The pressure dropped rapidly within the first 5 min in each run (Fig. 6). Repetition of the run with the identical catalyst resulted in a slower decrease of initial pressure, but led to an increase in the amount of ammonia collected in the trap (cf. filled circles which are referred to the right ordinate); associated with the latter fact, the material balance became better and its value tended to 80%. We can understand the phenomena as follows. Although the pretreatment desorbed almost all ammonia from the catalyst, those sites that could irreversibly adsorb ammonia were gradually filled. Thus, the material balance became higher.

The third run was considered as steady, since further repetition did not change the shape of the curve. The third run was adopted for further analyses (such as TPD and ESCA).

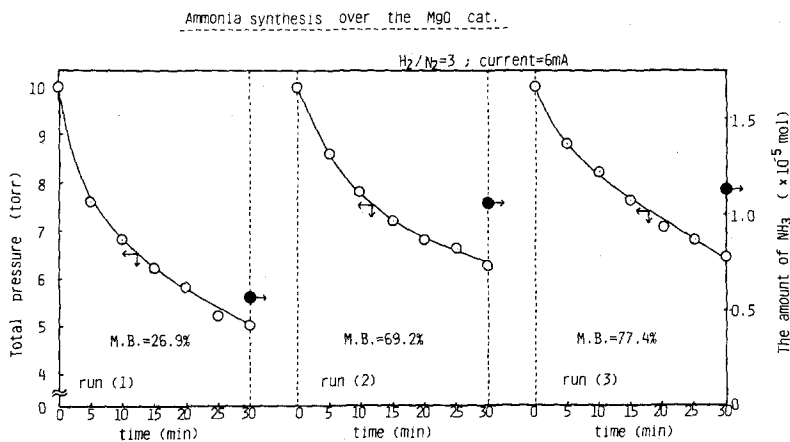


Fig. 6. Total pressure decrease with MgO catalyst.

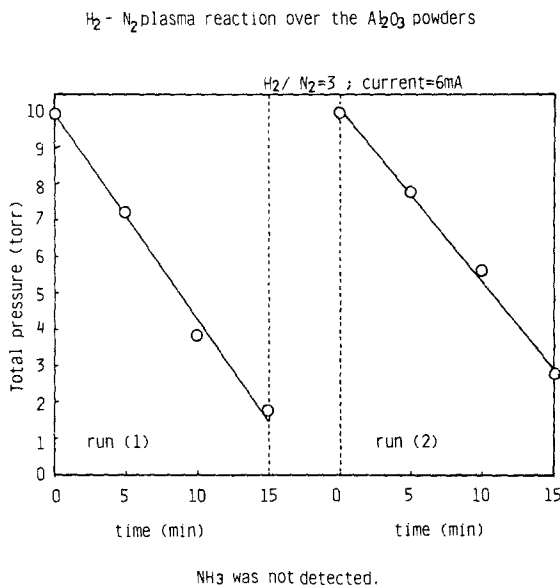


Fig. 7. Total pressure decrease due to ammonia formation over Al_2O_3 .

3.4. Reaction over Acidic Catalysts (Al_2O_3 , WO_3 , $SiO_2-Al_2O_3$)

The total pressure decreased so rapidly over acidic oxides, e.g., Al_2O_3 (Fig. 7), that within a quarter of an hour the total pressure became lower than 3 Torr. The experiment was abandoned due to the extinction of the plasma.

No ammonia, however, was detected in spite of the rapid decrease of pressure. The surface of alumina turned brown from its original white color. Some chemical change must have occurred to the alumina. Ammonia is an alkaline substance. It might have reacted with acidic alumina to form a complex. Behavior similar to alumina has been observed in $SiO_2-Al_2O_3$. WO_3 turned dark blue from its original yellowish green color after the reaction. It was partially reduced by hydrogen.

A trace amount of the gases in a liquid-nitrogen trap was analyzed with the QMA. Two peaks ($m/e = 26$ and 27) were observed; their ratio was 1:0.4. We assigned the peaks to HCN. Another peak ($m/e = 16$) in the residual gas was assigned to methane. The carbon source is supposed to be either CO_2 which was absorbed in the catalyst or grease from a stopcock.

3.5. TPD Spectra

Figure 8 and 9 show the TPD spectra of $MgO(A)$ and CaO . The peak of ammonia (solid line) lies at $130^\circ C$. The shapes of the peak are slightly

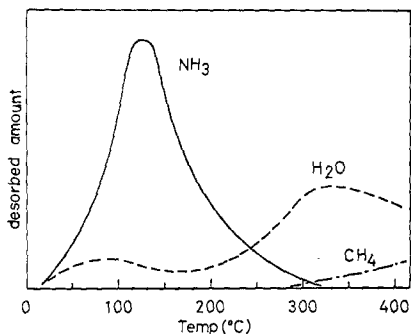


Fig. 8. Temperature programmed desorption (TPD) spectrum from MgO.

different between MgO(A) and CaO. The former is sharp, but the latter has a flat summit. The tail of MgO is broad and extends over 300°C. That of CaO, however, disappears above 250°C.

The profile of water is different between MgO and CaO. Water was desorbed from CaO over 200°C. The amount increased as the temperature rose. MgO showed two desorption peaks. One was broad and low, and had a peak at 80°C. The other resembled that of CaO, but had a maximum at 320°C.

Another desorbing species was observed in both catalysts. In MgO it appeared above 280°C. The desorbed gas had a mass (m/e) of 16 and was assigned to methane. In CaO a decreasing curve was observed below 150°C. The mass number was 26. We could not identify the gas. One of the most plausible candidates is HCN.

The TPD profile of alumina shows traces of ammonia and water above 300°C (Fig. 10). Adsorption of ammonia on alumina without plasma (Fig. 11) shows a peak of ammonia. The peak has its tail extending below 100°C.

3.6. ESCA Spectrum

An ESCA spectrum of MgO(A) was taken in order to detect nitrogen which was strongly adsorbed on the catalyst. The lower line in Fig. 12 is

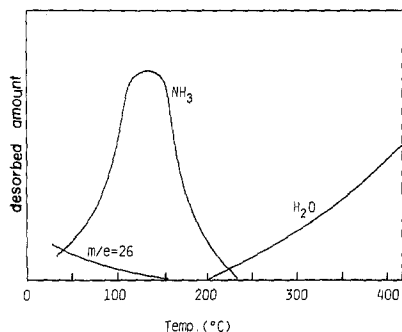


Fig. 9. TPD spectrum from CaO.

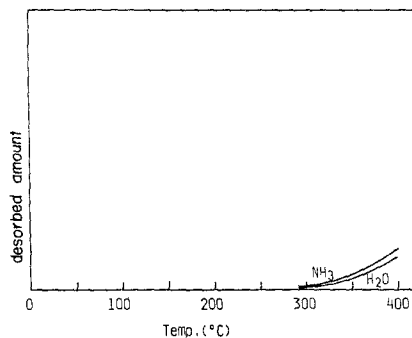


Fig. 10. TPD spectrum from Al_2O_3 .

the spectrum of freshly prepared MgO catalyst. There was no nitrogen on the catalyst.

The upper curve in Fig. 12 is the spectrum of MgO after the reaction. A peak of N 1s was observed at 399 eV. The amount of nitrogen calculated from the spectrum was too little to be assigned to a stable nitride (e.g., Mg_3N_2) left on the catalyst.

3.7. Metal Catalyst

The activity of metal catalysts was compared with that of the oxides. Figure 13 shows a reactor in which a bundle of metal tubes was placed. The metal tubes were a cathode and worked simultaneously as a catalyst. The surface area of the metal tubes was 80 cm^2 .

Figure 14 shows the total pressure change due to ammonia formation. Stainless steel (SUS) was the most active catalyst. In contrast to the acidic oxides (e.g., Al_2O_3), the pressure drop was not linear with the metal catalyst. This fact suggests that the ammonia formed was not absorbed, but adsorbed on the surface.

The Cu and the CuZn alloy catalysts were more active than MgO. Their activity was comparable to each other. Thus, Zn has little effect on the reaction.

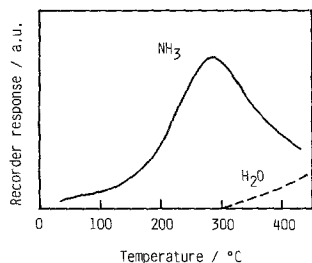


Fig. 11. TPD spectrum of ammonia adsorbed on alumina without plasma.

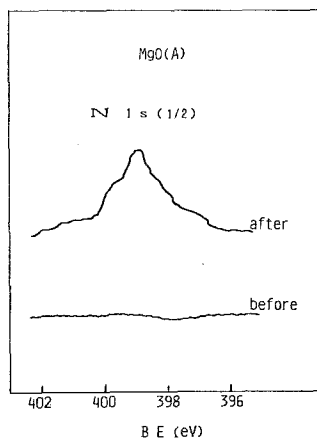


Fig. 12. ESCA spectrum of MgO. Before: freshly prepared MgO(A); after: MgO(A) after the reaction.

Aluminum seems to have no catalytic activity. We ascribe the inactiveness to an oxide layer which covers the metal surface. This layer cannot be removed even with a powerful discharge-cleaning with hydrogen.

4. DISCUSSION

The main process may be one of the following three.

- (i) Ammonia is formed in a plasma. It is adsorbed on a surface. When the adsorption is saturated, desorption occurs.
- (ii) The reaction occurs on the surface. Excited nitrogen molecules are adsorbed on the catalyst. The nitrogen is dissociated on it to become an adsorbed nitrogen atom $N(a)$, which in turn combines with hydrogen from the gas phase or on the surface to form successively $NH(a)$ and $NH_2(a)$, and finally to become ammonia which is desorbed from the surface.

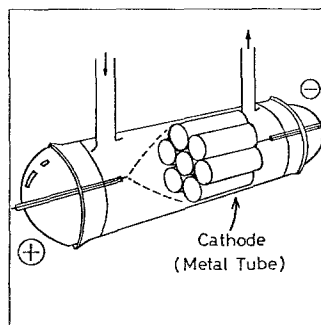


Fig. 13. Reactor for ammonia synthesis with metal tubes used simultaneously as catalyst and as cathode.

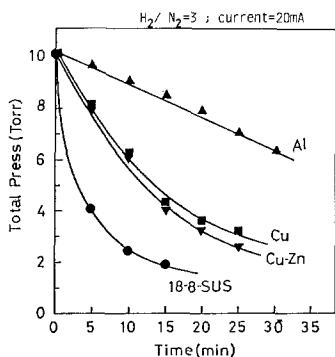


Fig. 14. Catalytic activity of metal catalysts.

- (iii) The nitride is formed. The excitation by plasma makes a nitrogen molecule so reactive that a catalyst surface easily becomes a nitride which is at the same time reduced by hydrogen atoms. The plasma reaction is a dynamical balance between nitriding and reduction to form ammonia.

The following experiment gives a clue to the question which of the processes was dominant. A H₂ gas or H₂/N₂ mixed gas was brought in contact with the MgO(A) catalyst as follows (Table I):

(a) First a H₂ plasma was put into contact with a pretreated MgO(A) catalyst. No pressure drop was observed.

(b) Then, the plasma was switched to a N₂ plasma. No pressure drop was observed.

(c) No ammonia could be detected after switching the plasma again to the H₂ plasma.

(d) A H₂/N₂ mixed gas (ratio 1/4) was introduced into the reactor. Ammonia was trapped in the liquid-nitrogen trap. Only ammonia could be detected in the trap to a significant amount.

Table I. Total Pressure Change of a H₂/N₂ Mixed Gas over the Magnesia(A) Catalyst under Plasma Conditions

Run	Atmosphere	$d\Delta P/dt^a$	Product
1	H ₂	0	Hydrocarbon
2	H ₂	0	—
3	H ₂	0	Hydrocarbon
4	H ₂ /N ₂ (1/4) (TPD measurement)	-0.46	Ammonia
5	H ₂	0	Hydrocarbon
6	H ₂ /N ₂ (3/1)		Ammonia

^a The rate of total pressure decrease in Torr/min.

(e) A TPD measurement was performed with the catalyst after process (d). The desorption of ammonia was observed (Fig. 8).

(f) A H_2 plasma was brought into contact with MgO(A) after the pretreatment. No pressure drop was observed to indicate the ammonia formation.

(g) A H_2/N_2 mixed gas (ratio 3/1) was introduced. A pressure drop was observed as in process (d).

We can explain the results of the experiment as follows:

1. No ammonia was formed by the contact of a pure H_2 or N_2 plasma with the catalyst.
2. Neither hydrogen nor nitrogen was adsorbed on the catalyst.
3. The fresh MgO surface was recovered with discharge cleaning of the H_2 plasma.
4. The nitrogen gas did not form a stable nitride with MgO during the reaction. The ESCA spectrum (Fig. 12) showed the presence of nitride, but the amount of nitride was negligible.

We conclude from the experiment that process (ii) is the main process occurring during the ammonia formation. The amount of nitride was so little that process (iii) cannot be the main process. If process (i) were the main process, then the plasma conditions (current, pressure, etc.) should be more important than the catalyst itself. No difference in the yield of ammonia would be exerted by the catalysts, since the wall effect depends only on wall temperature, and not on wall material.

5. CONCLUSION

The catalysis of metal oxide during ammonia synthesis under plasma conditions is different from that under thermal conditions; magnesia and calcia in the plasma reaction revealed a catalytic activity which is not observed in the thermal reaction.

The acidic oxides (e.g., Al_2O_3 and WO_3) showed more rapid pressure drop during the reaction than the basic oxides (MgO and CaO); no ammonia, however, could be collected in the liquid-nitrogen trap. A stable compound or complex may be formed between ammonia and the acid oxide.

Neither glass wool nor sodium chloride showed catalytic activity.

The above results are summarized in Table II.

Such metals as SUS (stainless steel), Cu, and CuZn alloy exhibited higher activity during the ammonia formation, but Zn and Al had no catalytic activity.

Table II. Ammonia Synthesis over Oxides (initial pressure 10 Torr; $H_2/N_2 = 3$; current = 6 mA)^a

Catalyst	r^b	Product
Blank	0.07	NH ₃
Glass wool	0.09	NH ₃
NaCl	0.09	NH ₃
MgO(A)	0.17	NH ₃
MgO(B)	0.21	NH ₃
CaO	0.14	NH ₃
Al ₂ O ₃	0.57	—
WO ₃ (H ₂ WO ₄)	0.20	(NH ₃)
SiO-Al ₂ O ₃ ^c	0.55	HCN ? and CN ₄ ? ^d

^a The substances in the first group show no catalytic activity. Those in the second and last groups are basic and acidic catalysts, respectively.

^b Rate of total pressure drop (for 0.8 g catalyst) in Torr/min.

^c Mole ratio SiO/Al = 87/13.

^d $m/e = 27$ and 16, respectively.

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