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Tubular membrane-like catalyst for reactor with dielectric-barrierdischarge plasma and its performance in ammonia synthesis

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Abstract

A membrane-like alumina tube was designed as a new type of catalyst for a reactor with plasma produced by dielectric-barrier-discharge. Anodizing the inner wall of an aluminum tube at dc 100 V using an oxalic acid solution formed an alumina film with straight pores of uniform size, each of which was developed independently and perpendicularly to the macroscopic surface. The gas-permeable membrane was obtained after chemical removals of the unanodized aluminum and the barrier layer on the outside. It was also confirmed that fine ruthenium particles were deposited on the pore walls of the alumina by immersing the tube in a saturated *n*-hexane solution of dodecacarbonyltriruthenium, followed by calcination and reduction. When the pure alumina membrane was introduced into nitrogen–hydrogen plasma, the ammonia yield was enhanced at each reaction condition. A further improvement was observed for the Ru-loaded catalyst. These results clearly indicate a synergistic effect of plasma and catalysis of the alumina and ruthenium on the ammonia synthesis. © 2004 Elsevier B.V. All rights reserved.

Keywords: Membrane-like catalyst; Anodic aluminum oxide; Plasma reaction; Ammonia synthesis; Ruthenium catalyst

1. Introduction

Since ammonia formation from nitrogen and hydrogen is exothermic [1,2], thermodynamic equilibrium theory indicates the superiority of a lower temperature for ammonia synthesis. Nevertheless, high temperatures (>670 K) are employed in the industry because a dissociative adsorption of dinitrogen, which is the rate-determining step in the catalytic process [1–3], takes place only very slowly when the temperature is lower than 573 K.

Nonequilibrium plasma has been studied as a promising way to obtain ammonia via NH radicals from N_2 -H₂ mixture at ambient temperature [4–7]. It has also been reported that the metals placed in plasma region or the metallic inner walls of the reactor chambers enhance the ammonia yield [7–14], indicating a synergistic effect of the metal catalysts and the plasmas. These types of experimental apparatus, however, were operated under reduced pressures (<15 kPa), so they are unsuitable for practical use.

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Dielectric-barrier-discharge is a simple technique for plasma generation at atmospheric or elevated pressures, and is applied to ozone generation and other reactions [15]. Because of a difficulty in introducing some solids into the limited plasma space, electrode surfaces are frequently desired to play catalytic roles in plasma-chemical processes [16–18], but their effects on conversion and selectivity are not necessarily significant. This is most likely due to the structure of the reactor in which reactant molecules do not have a very high probability of contact with the electrode of very small surface area.

This paper presents a new type of plasma-catalytic reactor, a dielectric-barrier-discharge system with a tubular membrane-like catalyst. Fig. 1 shows a schematic diagram of the reactor. The catalyst consists of a tubular alumina film with pores through which gases can pass. This system is expected to improve the efficiency of plasma reactions via the following advantages: (1) the catalyst is placed at the center of the plasma zone between the inner electrode and the quartz tube covered with the outer electrode, (2) contact of the plasma-excited molecules with the catalyst is considered to increase markedly because they are forced into the small pores, and (3) the membrane-like alumina can be

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Fig. 1. Schematic diagram of the plasma reactor with the tubular membrane-like catalyst.

easily loaded with various kinds of catalytic active species by the conventional procedures for catalyst preparation.

We prepared such a catalyst by an anodic-oxidation technique for surface finishing of aluminum. Applying dc voltage to aluminum as an anode in an aqueous solution of electrolyte such as sulfuric, oxalic, and phosphoric acid forms oxide films consisting of two regions: a porous layer and a barrier layer [19,20]. The porous layer comprises a uniform array of closed-packed hexagonal alumina cells, each containing a cylindrical pore formed perpendicularly to the macroscopic surface of the aluminum substrate. The barrier layer is a thin compact inner region lying adjacent to the metal. We have previously reported the preparation of the porous anodic film on an aluminum wire and its application as an electrically self-heated catalyst, the temperature of which can be instantaneously raised to initiate catalytic reactions [21,22]. In this study, we elaborated a tubular alumina membrane by the anodic oxidation of an aluminum tube and examined its catalytic performance in ammonia formation by the plasma at room temperature. Furthermore, ruthenium, which shows a high catalytic activity in thermal ammonia synthesis [1-3], was deposited on the alumina to evaluate a metal effect on the plasma reaction. As a result, notable synergistic effects of the catalysts and the plasma were observed.

2. Experimental

2.1. Preparation of tubular membrane-like alumina and loading of ruthenium

An outline of the preparation procedure of the tubular membrane-like alumina and Ru/alumina catalysts is illustrated in Fig. 2. The porous alumina was made from an aluminum tube with an external diameter of 5 mm, a thickness of 0.25 mm, a length of 125 mm, and a purity of 99.5%. Before anodizing, spontaneous oxide layers on the aluminum

substrate were removed by etching in a mixed solution of 5 wt.% sodium hydroxide and 0.5 wt.% sodium gluconate, followed by a dissolution of metallic impurities on the surface in a 1.8 wt.% nitric acid solution. An anodic film on the inner surface was formed by applying an anodizing voltage of +100 V from a dc power source (Kikusui Electronics, PAD110-5L) against a carbon-rod cathode (2 mm in diameter) placed at the center of the aluminum tube. During



Fig. 2. Preparation process of the tubular membrane-like alumina and Ru/alumina catalysts.

the anodization, an aqueous solution of 1 wt.% oxalic acid kept at 293 K was circulated through the inside of the tube. The tube was then washed with water and sealed at both ends with Teflon tape to protect the internal anodic film from damage during the following chemical treatments. Gas-permeability was obtained by dissolving the external unanodized metal in a 15 wt.% hydrochloric acid solution containing 0.1 mol/dm³ copper(II) chloride, followed by a dissolution of the barrier layer in a 25 wt.% phosphoric acid solution at 298 K. Loading of ruthenium onto the alumina membrane was carried out by adsorption of dodecacarbonyl-triruthenium from its saturated *n*-hexane solution at room temperature for 3 h. The prepared catalyst was calcined at 773 K for 4 h and then reduced at 673 K for 2 h before use.

2.2. Characterization

The porous structure of the membrane-like catalyst was examined with a scanning electron microscope (SEM, Hitachi S-900). A transmission electron microscope (TEM, Hitachi H-800) was also employed at an accelerating voltage of 200 kV for the pulverized sample to observe the ruthenium supported on the alumina. The amount of ruthenium was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Jarrell-Ash POEMS II) for a solution of the sample dissolved with aqua regia.

2.3. Ammonia synthesis by the plasma reactor equipped with the membrane-like catalyst

Plasma synthesis of ammonia was carried out at room temperature and atmospheric pressure by using the reactor illustrated in Fig. 1. The inner electrode was a stainless-steel tube of 4 mm diameter on which three holes of 1 mm were made at intervals of 30 mm. The membrane-like catalyst was fixed on the electrode with ceramic adhesive so as to cover the holes, and held at the center of a quartz tube (8 mm outside diameter and 1 mm thickness) with plastic tube-fittings. The outer electrode was a piece of aluminum foil (90 mm in length) by which the quartz tube was tightly surrounded. Discharge plasma was generated by applying an ac voltage at 21.5 kHz between the inner and outer electrodes with a power source (Logy Electric, LHV-13AC). The discharge voltage was adjusted in the range of 2.5-4.5 kV by controlling the primary-side ac voltage into the power source, and was continuously monitored with an oscilloscope (Iwatsu, DS-9242A) through a high-voltage probe. The electric energy consumed by the system was determined by an ac power meter at the primary side. N₂-H₂ mixture was introduced from the end of the quartz tube and led into the pores of the catalyst. The produced gases were taken out of the reactor through the holes on the central stainlesssteel tube, and analyzed on a gas chromatograph (Shimadzu, GC-8A) equipped with a 3m column of HayeSep C 60/80.

3. Results and discussion

3.1. Morphology of the membrane-like catalyst

In order to establish the optimum anodizing conditions, we prepared five kinds of oxide films by anodizing the internal walls of the aluminum tubes at 100 V for 3.3, 5, 10, 15, and 24 h. Fig. 3 illustrates a change in the film thickness with anodizing time. The thickness increased with time, but the growth gradually slowed down. SEM photographs of the internal surfaces are given in Fig. 4. Pores of uniform size were dispersed in the oxide at a pore-to-pore distance of about 170 nm and a pore population density of $4.9 \times 10^{13} \,\mathrm{m}^{-2}$, which were almost unchanged by the anodizing time. A long-time anodic treatment, however, resulted in a pore expansion and a decrease in the pore-wall thickness; the average pore diameter increased from 70 to 150 nm by extending the anodizing time from 3.3 to 24 h. This means that the anodic layer formed at the initial stage was chemically dissolved in the oxalic acid solution according to the pore-widening mechanism proposed by Nagayama et al. [23,24]. Because a partial disappearance of the pore walls and a union of the pores were observed after anodizing for 15 and 24 h, the oxide tube obtained for 10 h was employed for the plasma reaction. Its average pore diameter and film thickness were 120 nm and 95 µm, respectively.

Fig. 5a is a SEM photograph of the external wall of the tube after dissolving the unanodized aluminum. Rounded humps characteristic of the barrier layer were clearly observed. The cell size was about 260 nm, and hence the number of cells corresponding to the pore population density was calculated to be $1.7 \times 10^{13} \text{ m}^{-2}$, which was only about 35% of that on the inside. This is consistent with the reports on growth of the anodic film that, although a number of small pores were generated in the initial stage, only a fraction of the incipient pores continued to develop in the steady state where the anodic voltage and current were constant [25–28].

The metal-removed alumina tube was then immersed in the phosphoric acid solution to dissolve the outer alumina barrier. SEM images of the external surfaces in Fig. 5b–e



Fig. 3. Change in the thickness of the anodic oxide film formed at 100 V with anodizing time.



Fig. 4. SEM photographs of the internal walls of the aluminum tubes anodized at 100 V for (a) 3.3 h, (b) 5 h, (c) 10 h, (d) 15 h, and (e) 24 h.



Fig. 5. SEM photographs of the external walls of the alumina tubes anodized at 100 V for 10 h, followed by (a) a removal of the unanodized aluminum and an immersing in the phosphoric acid solution for (b) 20 min, (c) 40 min, (d) 60 min, and (e) 80 min.



Fig. 6. SEM photograph of the cross-section of the anodized tube in the vicinity of its external surface.

clearly demonstrate a disappearance of the barrier layer and an appearance of the pores with dissolution time. Most of the pores appeared after 40 min. A further soaking, however, resulted in a thinning or disappearance of the pore walls and fragility of the tube; therefore the immersing time was fixed at 40 min.

Fig. 6 shows a SEM photograph of a cross-section of the anodized tube in the vicinity of its external surface. It is found that the straight pores with a diameter of about 70 nm were developed independently of each other and perpendicularly to the macroscopic surface. The size and population density of the cells agreed with those estimated from Fig. 5a.

The tubular membrane-like Ru/alumina catalyst was obtained through an adsorption of $Ru_3(CO)_{12}$ onto the anodic film. No change in the porous structure of the alumina membrane was observed after the treatment. The Ru amount determined from the ICP-AES analysis was 0.10 wt.%, and hence 0.1 mg of ruthenium was supported on the alumina tube with a weight of 0.1 g. A TEM photograph of the pulverized catalyst is shown in Fig. 7. It clearly indicates that the Ru particles of 3–15 nm in diameter were deposited on the pore walls of the anodic film.



Fig. 7. TEM photograph of the pulverized Ru/alumina tube.



Fig. 8. Effects of the input voltage on (a) the yield and (b) the energy efficiency in the plasma synthesis of ammonia. The reactions were carried out at a H_2/N_2 ratio of 3 and a total flow rate of $30 \text{ cm}^3/\text{min}$.

3.2. Catalysis of the alumina and Ru/alumina membranes in ammonia synthesis by N_2 - H_2 plasma

3.2.1. Influence of the discharge voltage

Ammonia synthesis from N2-H2 mixture was carried out by using the plasma reactor with and without the membrane-like catalysts at room temperature and ambient pressure. Fig. 8a shows the amount of ammonia produced at a H_2/N_2 ratio of 3 and a total flow rate of $30 \text{ cm}^3/\text{min}$ as a function of effective alternating current voltage (rms). Ammonia was the only product; no hydrazine, N₂H₄, was detected. In the absence of the membrane, the ammonia yield was slightly raised with increasing voltage up to 3.5 kV, but it remained almost unchanged at a higher voltage. The maximum was 1.6×10^{-5} mol/min at 4.5 kV, which corresponded to a N₂ conversion of 2.4%. The electric power consumed by the system increased with input voltage: 51 ± 3 , 65 ± 3 , 84 ± 5 , 106 ± 6 , and 127 ± 9 W at 2.5, 3.0, 3.5, 4.0, and 4.5 kV, respectively. The energy efficiency estimated as the amount of NH₃ in moles per joule of energy consumption is shown in Fig. 8b. One of the reasons why the energy efficiency decreased with increasing voltage may be an occurrence of the backward reaction; at a higher voltage, more NH3 molecules were formed, but their decompositions to N2 and H2 were also promoted.

It is evident from Fig. 8a that introducing the tubular membrane-like catalysts into the N₂–H₂ plasma notably accelerated the ammonia production. Even the pure alumina showed an improvement in the ammonia yield by a factor of 1.5 at 4.5 kV. A further advancement was achieved by the Ru-loading; the ammonia generated at 4.5 kV was twice as much as that without the catalyst. An additional feature of the catalyst-equipped systems was that the yield tended to increase even beyond 3.5 kV. As the catalyst had little influence on the discharge current and the consumed electric power, the energy efficiency increased in the order of Ru/alumina > alumina > blank, as shown in Fig. 8b. These results clearly show that there were significant interactions of the plasma-excited molecules with the alumina and ruthenium.



Fig. 9. Effects of the flow rate on (a) the yield and (b) the energy efficiency in the plasma synthesis of ammonia. The reactions were carried out at a H_2/N_2 ratio of 3 and an input voltage of 4.5 kV.

Although the gas temperature at the outlet was almost the same as that at the inlet during the plasma discharge, the quartz tube and the central electrode of the reactor became hotter as the input voltage was raised. For example, the electrode temperature measured just after the reaction at 4.5 kV was about 573 K. We confirmed that no ammonia was generated by externally heating the reactor equipped with the Ru/alumina catalyst at 673 K, indicating that the plasma excitations of nitrogen and hydrogen were essential for the ammonia formation.

3.2.2. Influence of the flow rate

Fig. 9a illustrates the influence of the flow rate on the amount of ammonia produced at a constant voltage, 4.5 kV. The gas composition was kept at a H_2/N_2 molar ratio of 3. The Ru/alumina catalyst showed the highest yield at each flow rate, followed in order by the alumina and blank. The yield increased linearly with flow rate in the presence and absence of the catalyst. The power consumption was almost independent of the flow rate and the catalysts, and hence the energy efficiency also showed a liner increase with flow rate, as shown in Fig. 9b. The increases in the yield and the energy efficiency with increasing flow rate are probably due to a decrease in the decomposition of ammonia with decreasing resident time in the plasma region.

3.2.3. Influence of the gas composition

The effect of the reactant composition on the ammonia synthesis was also examined at a total flow rate of $30 \text{ cm}^3/\text{min}$ and a discharge voltage of 4.5 kV. The ammonia yield and the energy efficiency are plotted as a function of H₂/N₂ ratio in Fig. 10a and b, respectively. The yield increased in the order of Ru/alumina > alumina > blank at each gas mixing ratio. The same is also observed for the energy efficiency because the discharge current and the power consumption were little affected by the H₂/N₂ ratio and the membrane-like catalysts. It is noteworthy that there is a difference in the optimum gas composition between the plasma reactions with and without the catalysts; the yield and the energy efficiency increased with increasing H₂/N₂ ratio up to 5 when the catalyst was absent, whereas in the presence



Fig. 10. Effects of the gas composition on (a) the yield and (b) the energy efficiency in the plasma synthesis of ammonia. The reactions were carried out at a total flow rate of $30 \text{ cm}^3/\text{min}$ and an input voltage of 4.5 kV.

of the alumina and Ru/alumina catalysts, they reached a maximum at a H_2/N_2 ratio of 3, which is the stoichiometric value for ammonia synthesis. This suggests that a change in the major route of ammonia formation may occur due to installing the membrane-like catalyst into the plasma.

3.2.4. Speculations about the formation mechanism of ammonia

As shown in Figs. 8–10, the membrane-like catalysts appreciably promoted the ammonia formation, indicating that surface reactions on the alumina and ruthenium are important reaction pathways. However, because a significant quantity of ammonia was produced even in the absence of the catalyst, we cannot neglect other reaction processes.

It is widely known that NH radicals are generated by electron impacts of nitrogen and hydrogen [29–31]. Uyama and Matsumoto [5,6] and Matsumoto [7] have elucidated that the ammonia yield increases with amount of NH radical in the plasma bulk, indicating that the NH radical is a precursor of NH₃. They also found that NH₃ was formed by reactions between the NH radicals and H₂ molecules, but was decomposed by H atoms in the plasma.

Besides the noncatalytic plasma-phase reactions, we have to take into account an effect of the stainless-steel electrode placed at the center of the reactor. Matsumoto and coworkers [7,13,14] revealed that the amount of ammonia produced by radio-frequency or microwave discharge evidently increased with increasing number of iron and molybdenum wires placed in the plasma. This means that the metals behave as a catalyst in the plasma reaction. Similar catalytic effects have been reported for other metals such as stainless steel, platinum, and silver [7–12].

In the plasma reactor without the membrane-like catalyst, NH₃ was probably formed by both reaction processes: the chain reactions in the plasma phase and the surface reactions on the stainless-steel electrode. If the former is the main reaction, it is expected that, because electron energy in the plasma has a considerable influence on the amounts of NH radicals and H atoms, the ammonia yield will largely depend on the plasma power [6]. On the other hand, the external surface area of the stainless-steel tube in the plasma zone is so small (only 11.3 cm^2) that the latter reaction is likely restricted even if the excited molecules increase with input voltage. The fact that the effect of the discharge voltage on the ammonia yield was relatively small in the absence of the membrane (see Fig. 8) suggests a preponderance of the surface reaction on the stainless steel.

An interaction of nitrogen plasma with alumina has been studied by Kunimori et al. [32], who found from IR and TPD measurements that N₂ molecules were strongly chemisorbed on the Al₂O₃ surface without dissociation by the plasma excitation. It was also confirmed that the molecular N₂(ad) was hydrogenated to NH_x(ad) (x = 1-3) species by hydrogen exposure at room temperature when platinum was present on Al₂O₃. This is associated with a hydrogen spillover phenomenon: H(ad) atoms produced by dissociative adsorption of hydrogen on the Pt particles migrated to the Al₂O₃ surface, where they reacted with the N₂(ad) molecules to form the hydrogenated species.

Instead of the hydrogen spillover, atomic H(ad) species on alumina are also produced by hydrogen plasma even in the absence of metal [33]. Accordingly, the enhancement of the ammonia yield by the Ru-free alumina membrane may be attributable to the reactions of the N₂(ad) molecules and the H(ad) atoms on the alumina. However, we cannot eliminate a presence of the dissociated N(ad) species which has not been detected.

On the other hand, it has been reported that plasma-excited nitrogen is dissociated and adsorbed on ruthenium black to form N(ad) atoms, which are desorbed as NH₃ molecules by an atmospheric H₂ flow at room temperature [34]. This leads to a presumption that the Ru particles supported on the alumina membrane promoted a formation of atomic N(ad) species, and thereby increased the rate of ammonia production, as shown in Figs. 8–10. Spectroscopic studies about the reaction mechanism of nitrogen and hydrogen on the membrane-like alumina and Ru/alumina catalysts are in progress.

4. Conclusions

A tubular membrane-like catalyst was developed to raise the efficiency of reactions with plasma produced by dielectric-barrier-discharge. The alumina membrane prepared by the anodic oxidation and the subsequent chemical treatments of an aluminum tube had straight pores of uniform size through which gases passed. Introducing the alumina catalyst into N_2 – H_2 plasma evidently increased the ammonia yield, and a loading of ruthenium resulted in a further improvement. No change in the discharge current and the energy consumption due to the presence of the membrane was observed; therefore, the alumina and ruthenium are not modifiers of the plasma conditions but are catalysts to promote the ammonia formation via significant interactions with the plasma-excited molecules. This plasma-catalytic reaction system has some attractive features: it can be operated at atmospheric pressure and a variety of catalytic components can be easily deposited on the membrane, leading to an expectation of its practical application to other plasma reactions.

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