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One-step Ammonia Synthesis by In-liquid Plasma
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One-step ammonia synthesis under ordinary temperature and pressure has been attempted by introducing a nitrogen source (pure nitrogen gas or air) to hydrogen production reaction field of in-liquid plasma. As a result of the experiment, it was confirmed that ammonia can be synthesized by this method. However, the amount of ammonia synthesized was small. Most of the produced hydrogen is as pure. Also, the introduced nitrogen source is almost released outside of the reactor. This indicates low ammonia selectivity, study is required to improve the selectivity. The findings of this study are that the hydrogen production efficiency (HPE) and the C/O balance of the raw materials affect the amount of ammonia synthesized. It was found that the higher HPE the better. A one to one ratio of C and O was found to be the optimal condition.

液中プラズマ法による水素製造反応場に窒素源(純窒素ガスまたは空気)を導入し、水素製造からアンモニア合成までをワンステップで行う装置の開発を試みた。実験の結果、本手法でアンモニアを合成可能であることが確認された。しかし、アンモニア合成量は極微量だった。製造された水素はほとんどそのまま水素として回収される。また、導入された窒素源もほとんどがそのままリアクター外に排出される。これはアンモニアの選択率が低いことを示しており、今後選択率を向上させるための検討が必要である。本研究で得られた知見は、水素製造効率 (Hydrogen Production Efficiency; HPE) と原料の C:O 比がアンモニア合成量に影響を与えるということである。HPE が高ければ高いほどよく、C:O 比 = 1:1 が最適条件であることがわかった。

Key Words

In-liquid plasma, Hydrogen, Ammonia

1. Introduction

Ammonia (NH₃) is one of the most essential substances in modern society because it is used as a base chemical for a variety of products, perhaps most importantly for food fertilizer. Since the 19th century, the demand for ammonia has increased rapidly due to the increase in food demand accompanying population growth. In the 20th century mass production of ammonia was enabled through development of the Haber-Bosch process, which synthesizes ammonia from pure nitrogen and pure hydrogen at high temperatures and high pressures with an iron catalyst. This was a major achievement for a society which required a

massive food supply^{1)~5)}. Currently, the efficiency of Haber-Bosch method is 0.48 MJ/mol⁶⁾⁷⁾, and the combustion heat of ammonia is 0.38 MJ/mol⁸⁾. So, the energy efficiency of the current Haber-Bosch method reaches about 80% (0.38/0.48 $\approx$ 0.8), which is a very efficient method. However, a large amount of CO₂ is emitted in the manufacturing process of hydrogen. The hydrogen production method currently in practice is steam reforming of natural gas, and CO₂ is produced by the combination of oxygen in steam (H₂O) and carbon in natural gas. CO₂ emitted from ammonia synthesis accounts for about 1% of the world's total emissions, but most of this CO₂ is emitted by hydrogen production process^{9)~13)}. On the other hand, when hydrogen is produced by decomposing liquid hydrocarbons or alcohol using in-liquid plasma, the target is directly decomposed by the heat of plasma. No CO₂ is generated since no oxygen is involved in this process^{14)~16)}. In addition, no CO₂ is generated even

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though CO is generated in the case of alcohol decomposition. Although water electrolysis does not emit CO₂, the hydrogen production efficiency (HPE) of the in-liquid plasma method is up to twice that of water electrolysis^{17) 18)}. In addition, the HPE of the actual equipment with respect to the ideal HPE calculated from the standard enthalpy of formation has reached about 80% for electrolysis of water^{19) 20)}, whereas it is about 10 to 30% for plasma hydrocarbon decomposition and there is room for improvement^{18) 21)}. Therefore, there is a possibility that hydrogen will be produced more efficiently by future research. In addition, the in-liquid plasma method has the advantage that a reaction can be induced in an ordinary temperature and pressure environment with a simple and compact device. Therefore, this method is suitable for a distributed hydrogen production device^{16) 22) ~ 25)}. Considering the current situation in which 50% of hydrogen produced in the world is used for ammonia synthesis^{4) 26)}, it is advantageous to perform hydrogen production to ammonia synthesis in one step where ammonia is needed. This is because hydrogen and ammonia transportation costs can be suppressed. When nitrogen gas is introduced into the plasma reaction field, the bonds of nitrogen molecules can be broken by the energy of the plasma^{27) ~ 30)}. When nitrogen gas is introduced into the plasma reaction field for hydrogen production, it can be expected that ammonia will be synthesized by the combination of atomic hydrogen and atomic nitrogen. In other words, this is a distributed one-step ammonia (and hydrogen) production device that does not emit CO₂. Therefore, in this research, for the purpose of developing a distributed one-step ammonia production system without CO₂ emission, an experiment was conducted to introduce nitrogen gas into the in-liquid plasma hydrogen production reaction field, and the amount of ammonia synthesis and the amount of hydrogen synthesis were investigated.

2. Experimental method

Fig. 1 shows a schematic illustration of the experimental apparatus. The experimental apparatus consists of a high frequency power source, a reactor, a cylindrical electrode with an outer diameter of 6 mm and an inner diameter of 4 mm, a metal bubble holding plate, a gas cylinder for supplying pure nitrogen gas or air (as a nitrogen source), and a flowmeter. Copper was used for the electrode and the metal bubble holding plate. The reactor was filled with 125 mL of liquid, and nitrogen gas or air was supplied to the tip of plasma electrode at 0.3 L/min through the electrode. By applying a high frequency electrical voltage of 27.12 MHz to the electrode through a matching box, plasma was generated at the tip of electrode

Fig. 1 Schematic illustration of experimental apparatus

to synthesize ammonia. All experiments were performed at room temperature and at atmospheric pressure. Water, methanol, and ethanol were used as the liquid (as a hydrogen source), and the ammonia synthesis amount for each liquid was compared. The ammonia contained in the generated gas was recovered by dissolution in water or alcohol inside the reactor. After each experiment, the ammonia concentration in the water or alcohol was measured by ion-chromatography, then the ammonia production amount was calculated. In this experiment, the input power was 280 W and the duration of ammonia synthesis was 4 minutes.

3. Results and Discussion

As a result of the experiments, ammonia could be synthesized at several $\mu\text{mol}/\text{min}$. When the efficiency is calculated from this production rate, it is found to be a few mmol/MJ . Fig. 2 is a graph of the ammonia production amount and efficiency for each liquid. Fig. 2 shows confirmation that ammonia can be synthesized from various liquids with pure nitrogen or air as the nitrogen source under ordinary temperature and pressure conditions. This is an important result of this study. However, the efficiency is only a few mmol/MJ , which is very low considering that the efficiency of the Haber-Bosch method is about $2 \text{ mol}/\text{MJ}$. In this study when pure nitrogen is supplied, the maximum amount of ammonia synthesized was obtained with methanol. With water or ethanol, this amount almost fell to half that of methanol. When the nitrogen source was air, the ammonia synthesis amount for each liquid differed from that for pure nitrogen supply. In the case of water, the ammonia synthesis amount was reduced and in the case of ethanol, it was increased.

Next, composition of produced gas and hydrogen production in this research is described. Table 1 shows the composition of the produced gas when the hydrogen

Fig. 2 Ammonia production amount and efficiency for each liquid ingredient

Table 1 Composition rates of produced gas for each ingredient

Ingredient	Composition rate of produced gas					
	H ₂	CO	CO ₂	CH ₄	C ₂ H ₂	C ₂ H ₄
CH ₃ OH	0.65	0.32	0.00	0.02	0.01	0.00
CH ₃ OH + N ₂	0.67	0.30	0.00	0.01	0.01	0.00
CH ₃ OH + Air (N ₂ O ₂)	0.66	0.30	0.02	0.01	0.01	0.00
C ₂ H ₅ OH	0.66	0.29	0.00	0.05	0.00	0.00
C ₂ H ₅ OH + Air (N ₂ O ₂)	0.56	0.25	0.02	0.04	0.10	0.03

source is methanol or ethanol. When pure methanol was decomposed by in-liquid plasma without introducing a nitrogen source, the composition was H₂ 65%, CO 32%, and other light hydrocarbons such as methane 3%. No CO₂ was produced. This composition, where H₂: CO = 2: 1, is as expected from the chemical formula for methanol. Even if a nitrogen source was introduced, there was almost no change in the gas composition, and a gas mixture composed mainly of H₂ and CO was generated. However, when air was introduced, a small amount of CO₂ was produced. When air was supplied to ethanol plasma, H₂ decreased by 10% and CO decreased by 4% compared to the case of plasma decomposition of ethanol alone. In that case, 2% CO₂, 10% C₂H₂, and 3% C₂H₄ were produced. The production of CO₂ appears to be the effect of additional oxygen from the air. However, it is unclear why the production of light hydrocarbons increases when air is supplied, and it is a subject for further study. Whatever the case, even if air is supplied to ethanol, hydrogen and carbon monoxide are the main gas components. The value of “F_{pr} (flow rate of produced gas) = F_{ex} (flow rate of exhausted gas) - F_{NS} (flow rate of nitrogen source)” did not depend on the nitrogen source, but only on the type of liquid raw material. For example, in the case of methanol, the value is always F_{pr} = 0.55 L/min in the case of no nitrogen source, pure nitrogen, and air. For ethanol, it was F_{pr} = 0.50 L/min, and for water, it was F_{pr} = 0.05 L/min. This indicates that the input nitrogen is released outside of the reactor almost as is. This is consistent with the poor ammonia production efficiency

shown in Fig. 2. Perhaps, the production of nitrogen oxides and nitrogen carbide is also very small. The hydrogen production rate was calculated by multiplying the F_{pr} value by the hydrogen flow rate of the production gas, and the HPE was calculated from the hydrogen production rate.

As a result of the calculation, an HPE of 0.06-1.20 mol/MJ was obtained in present study. Since the input energy is the same in all experiments (280 W × 4 min = 67.2 kJ), this HPE is directly proportional to the hydrogen production rate. In order to evaluate this HPE, comparison was conducted with the HPE of other hydrogen production methods. Fig. 3 shows a comparison of the HPE obtained in this study and the HPE of other methods. Ref. 17 in Fig. 3 is the case where the in-liquid plasma method is optimized for hydrogen production. Ref. 19 is the actual HPE of the current water electrolysis. As can be seen from Fig. 3, when methanol is decomposed by in-liquid plasma, the HPE is 2 times higher than that of water electrolysis. However, in the present study, the HPE for methanol decomposition is lower by approximately half that of water electrolysis. Perhaps, this is because the nitrogen source consumed energy to become a nitrogen plasma. Also, the optimum shape of the plasma electrode is needle-shaped, which concentrates electric energy, but in present research, it is cylindrical in order to introducing a nitrogen source. This is the reason why discharge is less likely to occur and is considered to have affected the deterioration of the HPE. Also, from Fig. 1 and Fig. 2, it is clear that the ammonia produced per unit input energy is 10-4 times that of hydrogen, and

Fig. 3 Hydrogen production efficiency for each method

the selectivity is very low. Further, as described above, the fact that the introduction of the nitrogen source does not affect the flow rate of the manufacturing gas means that hardly any nitrogen has reacted. This is because if a large amount of ammonia is synthesized, it will not be recovered by replacement with water, and the gas flow rate should decrease. This also shows that the selectivity is low. Therefore, a significant improvement in selectivity is essential for this method. Introducing some kind of catalyst seems to be the most promising method, though methods are also being considered.

Regarding the amount of ammonia synthesized in this study shown in Fig. 2, it is considered that the ammonia synthesis amount depends on the HPE for the decomposition of the liquid ingredient and the C/O ratio of the nitrogen source and liquid. Since hydrogen is a raw material for ammonia, it is naturally considered that the larger the amount of hydrogen supply is, the better. On the other hand, since C and O are not ammonia raw materials, it is considered that for both, the less, is better. **Table 2** shows the chemical formulas, C/O balance of the liquid and the nitrogen source, and the HPE, for each liquid.

The C/O balance is the balance between the number of moles of carbon and the number of moles of oxygen. For example, since methanol is CH_3OH , when pure nitrogen is supplied (no additional oxygen supply) the ratio of C:O is 1 to 1, so even. When air is supplied, if it is assumed that the liquid ingredient and O_2 molecules react one-to-one, with C/O balance is O excess. When the C/O balance is even, C and O react 1 to 1 and become CO, thus C and O cancel

each other out. Therefore, the ideal C/O balance is even. The HPE shown in Table 2 were experimentally obtained, and they are the same values as shown in Fig. 3. In Table 2, methanol has the highest HPE and the C/O value is even. Therefore, it is considered that the highest ammonia synthesis amount was obtained with methanol as shown in Fig. 2. In Table 2, when switching from pure nitrogen supply to air supply, excess oxygen occurs due to the presence of methanol and water. Therefore, it is considered that the ammonia synthesis amount decreased. In the case of ethanol, by switching from a pure nitrogen supply to an air supply, the carbon excessive state shifts to a carbon excess relief state, and the ammonia synthesis amount improved by nearly double. For a pure nitrogen supply, in spite of the HPE for ethanol being 10 times or more greater than that of water, the ammonia synthesis amount is almost the same as that of water. The pure nitrogen and ethanol mixture creates a carbon excessive state. Therefore, it can be considered that the carbon excessive state has a greater suppressing effect on ammonia synthesis than an oxygen excessive state. In this experiment, N, H, O, and C are the reactive elements. Considering the reaction sequence based on the electronegativity and ionization energy, CO formation occurs first, and in the oxygen excessive state, all carbon is removed and N, H, and O remain. The next reaction in this state is the reaction of O and H. On the other hand, in the carbon excessive state, after CO formation, N, H, C undergo reaction with the next reaction in this state being that of N and C. As mentioned above, ammonia synthesis requires the most energy to cut N_2 bonds and to make

Table 2 Chemical formulas, C/O balance, and HPE for each liquid ingredient

Liquid ingredient	Chemical formula	C/O balance		HPE [mol/MJ]
		N_2 supply	Air(O_2) supply	
Water	H_2O	O excess	More O excess	0.06
Methanol	CH_3OH	even	O excess	0.95
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	C excess	C excess relief	0.86

2N. Therefore, it is considered that the ammonia synthesis amount is reduced because nitrogen is robbed by carbon in a carbon excessive state. It is considered that the amount of ammonia synthesis can be increase by adjusting the air supply rate or adjusting the C O balance to even using an appropriate liquid mixture.

Therefore, a similar ammonia synthesis experiment was performed using a liquid for which ethanol and water were mixed at a ratio of 1 to 1. When ethanol and water are mixed at 1 to 1, at 1 to 1 so that C O balance becomes even in the chemical formula, and it is considered that the amount of ammonia synthesis can be increase when supplying pure nitrogen. The ammonia production amount when the experiment was performed using a liquid in which ethanol and water were mixed at a ratio of 1 to 1 resulted in $5.0 \pm 0.1 \mu\text{mol}/\text{min}$. This is the highest value for the present study, and 20 % higher than when pure nitrogen was supplied to methanol (See Fig. 1). The reason for this is, as mentioned earlier, that the CO balance is even and at the same time, dependent on the HPE. The HPE in a liquid mixture of ethanol and water at a ratio of 1 to 1 was 1.1 ± 0.2 . This is the highest HPE for the present study, and approximately 10 % higher than that of the case of using methanol as a liquid raw material in the present study (See Fig. 2). Therefore, it is considered that the ammonia production amount became the highest.

4. Conclusion

To develop a device that can synthesis ammonia in one-step without CO₂ emission, a nitrogen source (pure nitrogen gas or air) was introduced into the hydrogen production reaction field of in-liquid plasma. As a result of the experiment, it was confirmed that ammonia can be synthesized by this method. However, the amount of ammonia synthesized was small only a few mmol/MJ. Most of the produced hydrogen is recovered as pure hydrogen. Also, the introduced nitrogen source is mostly released outside of the reactor. This indicates low ammonia selectivity, and further study is needed to improve the selectivity. The findings of this study are that the HPE and C O balance of the raw materials influence the amount of ammonia synthesis. It was found that the higher HPE the better. A one to one ratio of C and O was found to be the optimal condition.

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