Study of Zirconia Material Effect on H₂ Production from Ammonia-argon base Gas in Plasma Plate Type Reactor

Mostafa El-Shafie*, Shinji Kambara¹, Yukio Hayakawa¹ and Ryoma Sakai¹

1Gifu University, Environmental and Renewable Energy Systems Division, Graduate School of Engineering, 1-1 Yanagido, Gifu, 501-1193, Japan.
E-mail: mostafaelshafie81@gmail.com

Abstract. In this study, ammonia was decomposed into hydrogen and nitrogen gas by DBD plasma at different ammonia-argon gas base concentrations of 0.5% and 2% in plate type reactor. The effect of zirconia catalytic material on ammonia decomposition was investigated. Furthermore, it was found that the energy density has a positive effect on the outcome of hydrogen gas concentrations for both ammonia concentration experiments. Additionally, it was clear that hydrogen concentration increased with increasing plasma ammonia decomposition residence time. The hydrogen concentration results obtained by plasma-catalyst mode from ammonia concentration of 2% were much higher than that obtained from plasma only experiment. Also, the hydrogen concentration results at different input energy density for NH₃ decomposition with and without the zirconia catalyst system were compared. It can be concluded that the hydrogen concentration of the plasma-catalyst system was much higher than plasma only. It was observed that the addition of zirconia catalytic material into ammonia decomposition process was affected by the physical and electrical properties of the gas discharge. The energy efficiency of both ammonia concentrations experiments was compared, it was seen that the maximum energy efficiencies at NH₃ concentration of 2% was 0.1948% while at 0.5% NH₃ concentration was 0.084%.

1. Introduction

Hydrogen is often considered as an attractive alternative fuel to overcome the environmental issues. Hydrogen is a clean energy source and can be utilized in portable energy applications with water as the combustion by-product [1]. It can be produced by different renewable energy sources. However, the hydrogen economy is still limited due to the hydrogen storage inability in a safe and economical manner [2]. Hydrogen gas demands are recently growing which motivated the scientific researchers to improve hydrogen production technologies [3-8]. The DBD plasma can create excited and reactive species, which means that high electrons energy are generated allowing them to interact with the catalyst materials at milder temperatures and pressures. The synergistic between catalyst materials and plasma species have been studied to improve the decomposition process of different molecules such as steam reforming of methane, [9] dry reforming of hydrocarbons, [10-14], pollutant decomposition [10, 11], etc.

It has been reported the optical emission spectroscopy (OES) of NH₃ decomposition by dielectric barrier discharge plasma (DBD), it has been found that the OES of NH₃ was dominated by the band of the electronic excited NH₃* molecule, in range of 563.5–567 nm [15–18]. The decomposition of NH₃ gas by DBD plasma could be mainly achieved by the NH₃* species due to the other species weak band intensities of N₂*, NH*, H*.

\[ \text{NH}_3 + e \rightarrow \text{NH}_3^* + e \]  \hspace{1cm} (1)

\[ \text{NH}_3^* + e \rightarrow \text{NH}_2 + H + e \]  \hspace{1cm} (2)

...
NH₂ + e → NH + H + e             (3)

It was reported that ammonia decomposition by DBD plasma mainly activated to produce NH₃* species, then activated by an electron to generate NH₂ and NH species. The hydrogen and nitrogen gas can be generated from NH species through the following reaction [16],

NH + NH → N₂ + H₂                  (4)

In this study, we report the hydrogen production measurements from ammonia decomposition of DBD plasma-assisted catalysis on zirconia (ZrO₂) as well as plasma-only reactions to assess hydrogen production through DBD plasma process and distinguish between plasma-only and catalyst material surface contributions. The hydrogen concentrations at different input ammonia-argon base concentrations of 0.5% and 2% are determined. Furthermore, the effect of residence time on hydrogen production is also evaluated. The energy efficiency and output hydrogen flow rates of plasma-assisted zirconia catalytic material are compared.

2. Experimental setup
In this experiment, ammonia-argon base gas was fed at atmospheric pressure into the plate type reactor in a range of 0.1-1.0 L/min and plasma applied voltage ranges of 12-18 kV. The hydrogen production from Ammonia gas concentrations of 0.5% and 2% were monitored. The plasma plate reactor was filled with catalyst material type of zirconia materials, Table (1) shows zirconia material characteristics. While the DBD plasma was ignited in the electrode gap distance of 4.5 mm. Figure (1) shows the schematic diagram of plasma-catalyst assisted for hydrogen production from ammonia gas. Ammonia gas was fed into the plate reactor and was controlled by the mass flow controller. The decomposed gas samples were taken using a syringe and then analyzed by the gas phase chromatography (GC). Also, the hydrogen concentration measurements were carried out for the plate reactor with and without adding zirconia catalytic material to evaluate the catalyst material effect on ammonia decomposition into H₂ and N₂ gas.

| Diameter (mm) | Density (g/mL) | Relative static permittivity (at 10 kHz) | Mass (g) | Volume (L) |
|---------------|----------------|----------------------------------------|----------|------------|
| 1             | 6.07           | 20-24                                  | 36       | 0.00593    |

Table 1. Characteristics of zirconia catalyst material.

Figure 1. Schematic diagram of experimental setup.
3. Results & discussions

3.1 Zirconia effect on H2 production from 0.5% NH3-Ar base gas

Ammonia gas is an important hydrogen energy carrier, additionally, ammonia has no environmental impact because ammonia is carbon-free. Ammonia gas is decomposed by non-thermal plasma or atmospheric to produce hydrogen and nitrogen gas. Zirconia (ZrO2) catalytic material is used to enhance hydrogen production from ammonia gas. The most interesting observations have been registered where the DBD plasma reactor is filled with the spherical beads of a high dielectric material such as ZrO2; it can enhance the electric fields at the points of contact between the beads will lead to getting higher concentrations of excited species [19, 20]. Also, it has been reported that the nature of catalyst surface can have an effect on the electric field, and irregularities such as surface roughness or the presence of surface pores can make variations in the electric field and some of the local regions of field intensification can become a high-energy electrons source [21]. The decomposed gases were analyzed by gas phase chromatography (GC), while the outlet gases are collected using a syringe. The conversion rate is determined according to the following expression: conversion rate [%] = H2

\[
\text{conversion rate [%]} = \frac{\text{H}_2 \text{ concentration [%]}}{(\text{NH}_3 \text{ concentration [%]} \times 1.5)} \times 100.
\]

Figure (2) demonstrates the H2 conversion rate of ammonia gas at different plasma applied voltage and input ammonia flow rates. It was found that the conversion rate increased with plasma voltage at all ammonia input flow rates. Also, the maximum conversion rates of 66.85 %, 33.66%, 26.47% were obtained at ammonia input flow rate of 0.1, 0.5, 1 L/min and plasma voltage of 18 kV, respectively. Furthermore, it was observed that the GC chemical species results included H2, N2, O2 and unreacted ammonia gas. Moreover, there is a positive contribution of the zirconia packing material on the conversion obtained, because of the plasma electric field enhancement at the contact points, but a negative contribution due to the lower residence time of the high ammonia gas flow rates.

Figure (3) shows the hydrogen concentration at different energy density and feeding ammonia flow rates. The energy density (Ed) is calculated according to the following relation:

\[
E_d = \left(\frac{1000 \times P}{v}\right) \times t,
\]

where P is the input power [W], v is the reactor volume [cm3], and ammonia decomposition residence time [s]. It was found that the hydrogen concentration increased with the energy density increased. Also, it was observed that the maximum obtained hydrogen concentration was 0.499% at ammonia input flow rate of 0.1 L/min and energy density of 69.6 J/cm3. It was clear that the best results were obtained at low NH3 input flow rate due to high energy density. Figure (4) shows the residence time effect on hydrogen production from ammonia decomposition at DBD plasma applied voltage of 18 kV. It was clear that residence time was an important factor for ammonia decomposition into hydrogen and nitrogen gas which appeared with increasing ammonia input flow rate. It can be concluded that residence time has a negative effect on the hydrogen production from ammonia decomposition by DBD plasma influencing the retention time which changes the electric field distribution and plasma reactivity.

3.2 Zirconia effect on H2 production from 2% NH3-Ar base gas

To understand ammonia decomposition using plasma-catalysts, it is important to ammonia decomposition reaction mechanism which is initiated by the adsorption of ammonia molecules onto the active site surface. These adsorbed ammonia molecules undergo successive N–H bond cleavage, releasing hydrogen atoms that can combine to form molecular hydrogen [22]. Neyts and Bal [23] have recently investigated that the catalytic material addition to a plasma discharge can improve the plasma electric field influencing the species retention time at the catalyst material surface and increasing the surface reactivity. Moreover, the catalyst materials will yield more electrical energy when materials of higher dielectric constant are used resulting in the formation of more electrons of higher energy which increased the ionized and excited species. In this work, the effect of the ammonia feeding gas concentration on hydrogen production was investigated. Also, zirconia catalytic material was utilized to fill the plasma plate reactor type. Ammonia –argon base gas with a concentration of 2% was fed into the reactor at 0.1 L/min and atmospheric plasma voltage range of 12–18 kV.
Figure 2. The effect of plasma voltage on H\textsubscript{2} conversion at different NH\textsubscript{3} flow rates.

Figure 3. Energy density effect on H\textsubscript{2} concentration at different NH\textsubscript{3} flow rates.

Figure 4. Residence time effect on hydrogen concentration at plasma voltage of 18 kV.
Also, this experiment is carried out without catalyst materials to declare zirconia catalytic material effect on the hydrogen production from ammonia-Ar gas base at different plasma applied voltage. Ammonia-Ar base experiment was carried out with and without filling the plate reactor with zirconia catalytic material. Figure (5) illustrates the hydrogen conversion rate results of both experiments with and without adding zirconia catalytic material. It was found that H$_2$ conversion rate increased with the plasma applied voltage increased. Also, the conversion rate results of ammonia decomposition experiment with adding zirconia catalytic material have higher values than ammonia decomposition experiment without catalyst material. It can be concluded that zirconia material can be utilized to enhance ammonia decomposition using DBD plasma. To clarify the catalytic material effect on H$_2$ production from ammonia gas, the hydrogen concentration versus the energy density is shown in figure (6). It was observed that the hydrogen concentration enhanced by the addition of zirconia catalytic material to the ammonia decomposition system by DBD plasma. It was clear that the ammonia gas molecules are absorbed by zirconia material active surface producing higher electron energy.

Figure 5. Comparison of zirconia catalyst effect on H$_2$ conversion rate from 2% NH$_3$.

Figure 6. Comparison of H$_2$ concentrations with and without zirconia catalyst at different energy density.

3.3 Evaluation of ammonia-Ar base gas decomposition by DBD plasma

To assess the decomposition process of the ammonia-Ar gas base at different concentrations by the DBD plasma, the hydrogen flow rate was determined at an input flow rate of 0.1 L/min and at
different input electric power. A comparison between the hydrogen flow rates results of ammonia input concentrations of 0.5 & 2% was described in figure (7). It was found that the hydrogen flow rate increased with the input power for both ammonia input concentrations. However, the hydrogen flow rate results of the ammonia input concentration of 2% were higher than lower input ammonia concentration at different input electric power. In addition to the catalyst effect on ammonia decomposition by DBD plasma, it can be concluded that the hydrogen production will also depend on the plasma input power. The energy efficiency of the DBD ammonia decomposition process will also depend on the catalyst material structural features such as its morphology, porosity, and chemical activity as well as plasma nature. Figure (8) compares the energy efficiency results of both ammonia experiment concentrations at different electric power. It was clear that energy efficiency increased with increasing plasma input power. Furthermore, it was found that the maximum energy efficiency obtained at NH3 concentration of 2% was 0.1948 % while at 0.5% NH3 concentration was 0,084%.

4. Conclusion
Ammonia-argon base gas was decomposed into hydrogen and nitrogen gas by DBD plasma at different ammonia-argon gas base concentrations of 0.5% and 2% were investigated. The effect of zirconia catalyst material on ammonia decomposition was studied. It was found that the NH3 conversion rate was significantly increased when DBD plasma was combined with the catalyst. Furthermore, it was observed that the energy density has a positive effect on the produced hydrogen gas concentrations of both ammonia concentrations experiments. Additionally, it was clear that
hydrogen concentration increased with ammonia decomposition reaction time or residence time increase. The NH$_3$ conversion and hydrogen concentration obtained by plasma-catalyst mode from ammonia concentration of 2% were much higher than those obtained using plasma only. Also, it was compared the hydrogen concentration results at different input energy density for NH$_3$ decomposition with and without zirconia catalyst. It was found that the hydrogen concentration of plasma-catalyst system was much higher than plasma only system. An evaluation of plasma-catalyst system was developed to compare different ammonia input concentrations. In general, adding zirconia catalytic material into the ammonia decomposition process by DBD plasma will affect the physical and electrical properties of the gas discharge which causes some modification to the produced hydrogen and nitrogen gases of the plasma-catalytic processes. The energy efficiency results of both ammonia concentrations experiments were compared. It was seen that the maximum energy efficiency obtained at NH$_3$ concentration of 2% was 0.1948 % while at 0.5% NH$_3$ concentration was 0.084%.

5. References

[1] Yin SF, Xu BQ, Zhou XP, Au CT (2004) Appl Catal A Gen 277:1–9.
[2] Hill A, Torrente L (2014) Murciano. Int J Hydrog Energy 39:7646–7654.
[3] Rosen, M. A.; Scott, D. S. Comparative efficiency assessment for a range of hydrogen production processes. Int. J. Hydrogen Energy 1998, 23, 631-640.
[4] L. Barelli, G.Bidini, F.Gallorini, S.Servili, Hydrogen production through sorption-enhanced steam methane reforming and membrane technology: a review, Energy 33(2008)554–570.
[5] Shiga, H.; Shinda, K.; Hagiwara, K.; Tsutsumi, A.; Sakurai, M.; Yoshida, K.; Balgen, E. Large scale hydrogen production from biogas. Int. J. Hydrogen Energy 1998, 23, 631-640.
[6] J. D. Holladay, J. Hu, D. L. King, Y. Wang, An overview of hydrogen production technologies, Catal. Today 139 (2009) 244-260.
[7] M. El-Shafie, S. Kambara, Y. Hayakawa, T. Miura. Preliminary results of hydrogen production from water vapor decomposition using DBD plasma in a PMCR reactor. Int. J. Hydrogen Energy, 2019, 44: 20239-48.
[8] M. El-Shafie, S. Kambara, Y. Hayakawa, Hydrogen Production Technologies Overview. Journal of Power and Energy Engineering 7(2019) 107-154.
[9] Nozaki, T.; Okazaki, K. Non-thermal plasma catalysis of methane: Principles, energy efficiency, and applications. Catal. Today 2013, 211, 29–38.
[10] Allah, Z. A.; Whitehead, J. C. Plasma-catalytic dry reforming of methane in an atmospheric pressure AC gliding arc discharge. Catal. Today 2015, 256, 76–79.
[11] Gallon, H. J.; Tu, X.; Whitehead, J. C. Effects of Reactor Packing Materials on H 2 Production by CO 2 Reforming of CH 4 in a Dielectric Barrier Discharge. Plasma Processes Polym. 2012, 9, 90–97.
[12] Tu, X.; Gallon, H. J.; Twigg, M. V.; Gorry, P. A.; Whitehead, J. C. Dry reforming of methane over a Ni/Al2O3 catalyst in a coaxial dielectric barrier discharge reactor. J. Phys. D: Appl. Phys. 2011, 44 (27), 274007–274007.
[13] Tu, X.; Whitehead, J. C. Plasma-catalytic dry reforming of methane in an atmospheric dielectric barrier discharge: Understanding the synergistic effect at low temperature. Appl. Catal., B 2012, 125, 439–448.
[14] Kim, J.; Abbott, M. S.; Go, D. B.; Hicks, J. C. Enhancing C–H Bond Activation of Methane via Temperature-Controlled, Catalyst– Plasma Interactions. ACS Energy Lett. 2016, 1 (4), 94–99.
[15] Watson, J. K. G., & Majewski, W. A. (1986). Assignment of the schuster band of ammonia. Journal of Molecular Spectroscopy, 115, 82–87.
[16] Agostino, R., Cramerossa, F., Benedictis, S. D., & Ferraro, G. (1981). Kinetic and spectroscopic analysis of NH3 decomposition under R.F. plasma at moderate pressure. Plasma Chemistry and Plasma Processing, 1, 19–35.
[17] Cicala, G., De Tommaso, E., Raino, A. C., Lebedev, Y. A., & Shkhatov, V. A. (2009). Study of positive column of glow discharge in nitrogen by optical emission spectroscopy and numerical simulation. Plasma Sources Science and Technology, 18, 025032.
[18] Nicholas, J. E., Spiers, A. I., & Martin, N. A. (1986). Kinetics and mechanism in the decomposition of NH3 in a radio-frequency pulse discharge. Plasma Chemistry and Plasma Processing, 6, 39–51.

[19] Zhang, Y., Wang, H., Jiang, W., & Bogaerts, A. (2015). Two-dimensional particle-in cell/ Monte Carlo simulations of a packed-bed dielectric barrier discharge in air at atmospheric pressure. New Journal of Physics, 17, 083056.

[20] Koen Van, L., & Annemie, B. (2016). Fluid modelling of a packed bed dielectric barrier discharge plasma reactor. Plasma Sources Science and Technology, 25, 015002.

[21] Butterworth, T., Elder, R., & Allen, R. (2016). Effects of particle size on CO2 reduction and discharge characteristics in a packed bed plasma reactor. Chemical Engineering Journal, 293, 55–67.

[22] Hansgen DA, Vlachos DG, Chen JG (2010) Nat Chem 2:484–489.

[23] Neyts, E. C., & Bal, K. M. (2017). Effect of electric fields on plasma catalytic hydrocarbon oxidation from atomistic simulations. Plasma Processes and Polymers, 14, 1600158.

Acknowledgments
The authors would like to thank Prof. Shinji Kambara (Environmental and energy systems department-Gifu University-Japan) for his continuous support.