Ammonia decomposition by heating of a single-mode microwave irradiation for rapid production of hydrogen

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Abstract: Ammonia decomposition was carried out by using a microwave heating for rapid production of hydrogen. For the uniform heating of supported metal catalyst, single standing wave was generated in the cylindrical microwave cavity, in which the electric field was concentrated at the catalyst bed settled in the center of the cavity. In this system, time of heating up to 600 ℃ was less than 15 s over 5%Co/Al_2O_3 catalyst, which is suitable for both of the microwave heating and catalytic activity for ammonia decomposition. Efficiency of microwave heating was improved by addition of SiC powder with catalyst.

Keywords: ammonia, hydrogen, microwave.

1. Introduction

Ammonia is one of the candidates for the energy carrier material which contains hydrogen to transport and store. The main features of ammonia are as follows: high hydrogen content (17.7 wt%), easiness of transportation as liquid ammonia, and no emission of carbon dioxide. Decomposition of ammonia to produce hydrogen, however, needs high temperature over 300 ℃ owing to the equilibrium limitation by the endothermic reaction. To widely use of ammonia, such as an on board reforming for fuel cell system, small size reactor for rapid generation of hydrogen will be essential in future.

For the development of the efficient reactor system, we have examined microwave heating for the decomposition of ammonia. Although microwave heating allows for rapid and selective heating of the target material by the dielectric heating mechanism, commercially available microwave reactor with a multi-mode irradiation is not suitable for the continuous flow type reaction with solid catalysts, because of the disordered microwave intensity in the electromagnetic field. To overcome the problem, a single-mode microwave irradiation system with a cylindrical cavity was developed for the flow reaction [1, 2]. In this system, microwave is radiated as a single standing wave, and the electric field in concentrated at the quartz tube settled in the center of the cavity, causing uniformly heating of the solid catalysts in the tube (Fig. 1). The aims of this study are i) investigation of optimal reaction condition and catalyst for ammonia decomposition under microwave irradiation, and ii) confirmation of rapid heating and hydrogen production by this system.

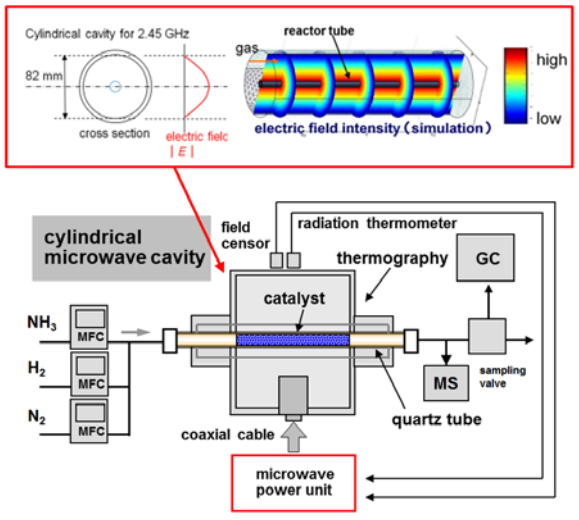

Figure 1. Schematic illustration of single-mode microwave irradiation apparatus for a continuous gas flow.

2. Experimental

Ni, Co, Fe/γ-Al_2O_3 supported catalysts with loading amount of 1-20 wt% were prepared by the impregnation method. The particle size was sieved as 250-500 μm. All catalysts were reduced by pure hydrogen at 600 ℃ before the reaction. Figure 1 shows a schematic of the reaction system and microwave

power unit. The diameter of the cylindrical cavity was based on the wavelength of the incident microwave in order to form a single standing wave. Microwave was generated by a solid-state power amplifier, which can vary both the microwave power (0-100 W) and frequency (2.3- 2.7 GHz). These electric properties were PID controlled automatically by feedback of the information about field sensor and radiation thermometer. For the reaction, pure NH_3 (40 ml/min) was fed into the quartz reactor tube filled by the catalyst (100 mg). In some reactions, 10 mg of SiC powder was mixed with the catalyst to support the microwave heating. Products were analyzed by two on-line gas chromatographs or mass spectroscopy.

3. Results and discussion

Table 1 summarizes the reaction results of ammonia decomposition under microwave heating. Most of catalysts are well heated over 500 ℃ by microwave irradiation in the cylindrical cavity. During the reaction, the dielectric property of catalyst was influenced by the temperature, atmosphere and the deterioration of catalyst. By control of the both frequency and power, single-standing wave was constantly formed in the cavity, causing the constant heating of the catalyst. To elucidate the microwave heating property, loading amount of Co was varied from 1% to 20%, because metallic materials generally reflect a microwave. Although the catalytic activity increased with increasing the loading amount of Co, 20% Co/Al_2O_3 could not be heated up to 550℃ by 100W of microwave output. It indicated that the catalyst metal with high loading amount reflects the microwave because of the large size metal particles. 5-10% of Co loading is proper amount to combine easiness of microwave heating and catalytic activity. The order of activity was Co>Ni>Fe at 450C with mixing of SiC. Note that the addition of SiC for 5% Co/Al_2O_3 caused not only decrease of microwave output from 99 W to 25W but also increase of conversion reached to 99 % at 550℃.

Table 1. Summary of NH_3 decomposition by MW heating

catalyst	SiC mixing	conversion (%)		microwave output / W	
		450 C	550 C	450 C	550 C
1%Co/Al_2O_3	——	2.8	20.4	72	86
5%Co/Al_2O_3	——	31.8	85.4	74	99
10%Co/Al_2O_3	——	39.0	93.9	94	63
20%Co/Al_2O_3	——	42.8	—— *	99	—— *
5%Co/Al_2O_3	10 mg	48.1	99.0	23	28
5%Ni/Al_2O_3	10 mg	42.4	98.9	14	23
5%Fe/Al_2O_3	10 mg	36.9	97.4	16	28

* sample was not heated under 100W power

Cold start property up to 600℃ over 5% Co/Al_2O_3 with SiC was exhibited in Fig.2. When the reaction was start, the microwave power was well controlled from 0-100W (Fig. 2a). The temperature reached to 500℃ for 7 s, and 600℃ for 15s. After reaching the preset temperature, the temperature was well stabilized at 600C. Formation of hydrogen and nitrogen was confirmed at 5s after the reaction start (Fig. 2b), and it reached to constant for 15s. The heating profile can be varied by changing the PID parameter. These results demonstrated that the microwave heating has potential for the rapid production of hydrogen from ammonia.

4. Conclusions

Microwave heating with cylindrical cavity was apply to the ammonia decomposition. Heating time up to 600℃ was less than 15 s over 5% Co/Al_2O_3, suggesting the potential of this system for the rapid production of hydrogen from ammonia.

References

1. M. Nishioka, M. Miyakawa, H. Kataoka, H. Koda, K. Sato, T. M. Suzuki, Nanoscale, 3 (2011) 2621.
2. K. Sato, M. Nishioka, M. Kasai, H. Higashi, M. Natsui, T. Inoue, Y. Hasegawa, Y. Wakui S. Hamakawa, T. M. Suzuki, Trans. Mater. Res. Soc. Jpn., 36 (2011) 221.

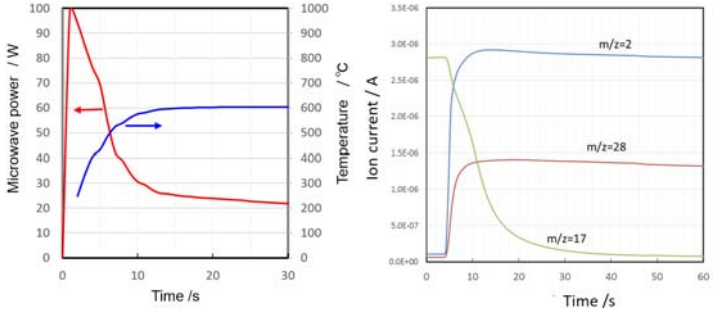

Figure 2. Cold start test of NH_3 decomposition over 5%Co/Al_2O_3 with SiC, (a): MW power and temperature, (b): products analysis by MS.