Reforming of Methane Using Single-mode Microwave Irradiation Heating in a Cylindrical Cavity

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For the application of microwave heating to a continuous gas-flow type reaction using a solid catalyst, a cylindrical cavity system was used for reforming reaction of methane. A single standing microwave was generated within the cavity, resulting in uniform heating of the reaction tube positioned in the center of the cavity. Heating tests were conducted with different loadings of Pd/Al₂O₃ catalyst. Following hydrogen reduction, 5-10 wt% catalyst loading achieved the best heating effect and avoided reflection of microwaves. Reforming reactions were then conducted over 5 wt% Pd/Al₂O₃ catalyst using microwave heating and conventional heating, respectively. The conversion efficiency of methane for both steam reforming and dry reforming was higher by microwave heating than by conventional heating. In addition, microwave heating of the Ni/γ-Al₂O₃ catalyst restricted coke deposition attributed to direct dielectric heating by the microwave irradiation promoting carbon combustion. The results demonstrate the advantages of this microwave heating system for flow-type reactions using a solid catalyst.

Keywords
Microwave heating, Standing wave, Methane, Steam reforming, Dry reforming

1. Introduction

Microwave irradiation directly heats the component molecules of a substance, resulting in rapid and high efficiency heating compared to the convection and conduction of the common approach of electric furnace heating. The use of microwave heating for chemical reactions has been widely studied, finding that synthesis time is significantly shortened and reactivity is improved\(^{(10)}\). Most previous studies have examined batch-type reactions in the liquid phase. However, the microwaves are irregularly reflected within the irradiation space (cavity), so the electric field intensity is non-uniform. Therefore, stirring is necessary for uniform heating of a solvent in the liquid phase. Stirring is difficult in a flow-type reaction, so previous studies have examined various microwave irradiation methods to uniformly heat the fluid. One method is the use of a standing wave\(^{(11)}\). If a standing wave can be formed in the cavity, it is possible to heat the fluid uniformly during the flow reaction by installing the reaction tube at the location where the electric field intensity is the greatest. Fukushima reported the ethanol reforming by using a single-mode standing wave within a cuboid microwave cavity achieved hydrogen production at relatively low temperature\(^{(13)}\). Tsubaki et al. reported the combination system of the operando Raman spectroscopy and single-mode microwave heating for solid catalysts with cuboid cavity\(^{(14)}\). It is for the investigation of a microwave enhanced solid catalyst reaction. Nishioka et al. have studied a chemical reaction using a cylindrical microwave cavity with single-mode standing wave\(^{(15)}\). For example, using a microwave of frequency 2.45 GHz with a cavity of diameter 82 mm generates a standing wave with the electric field distribution in the diameter direction (Fig. 1). The electric field is concentrated at the center along the long axis of the cavity. The intensity is constant along the long axis (TM010 microwave irradiation mode), so a reaction tube installed at the center can be heated uniformly. Precise control of the microwave frequency is important to generate a stable standing wave. Magnetron generators are widely used in various microwave applications, but do not allow precise output adjustment. The semiconductor-type oscillator enables precise feed-back control of the microwave output and frequency, and therefore, a stable standing wave can be maintained even if the dielectric properties change due to the temperature or composition of fluid during the reaction.
Consequently, this system is effective for synthesizing nanoparticles and organic materials\(^\text{15,17}\).

The present study employed this cylindrical reaction tube system for heating solid catalysts in a gas-flow type reaction. The microwaves were uniformly concentrated on a reaction tube with solid catalyst placed in the center of a cylindrical cavity, and then heated for use in a methane reforming reaction. Steam reforming and dry reforming of methane are important reactions for producing synthesis gas and hydrogen\(^\text{18,22}\).

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 \quad (1) \\
\text{CH}_4 + \text{CO}_2 & \rightarrow 2\text{CO} + 2\text{H}_2 \quad (2)
\end{align*}
\]

The two reactions shown in Eqs. (1) and (2) are highly endothermic. Consequently, restriction of thermodynamic equilibrium and reduction of the temperature at the catalyst bed may occur during the reaction. In addition, deposition of coke on the catalyst surface during the reaction impairs the long-term catalytic activity.

Many methods have been evaluated to enhance the catalytic activity, such as a catalytic membrane reactor and electrical promotion of the reaction. As membrane reactors, Pd based metal membrane\(^\text{23}\), solid electrolyte\(^\text{24}\) and porous membrane such as zeolite\(^\text{25}\) were used to subtract hydrogen from the products for shift the thermodynamic equilibrium. Several methods of electrical promotion were reported, such as microwave plasma\(^\text{26,27}\), corona plasma\(^\text{28}\), arc plasma\(^\text{29}\), dielectric barrier discharge plasma\(^\text{30,31}\), thermal plasma\(^\text{32}\), electric field\(^\text{33,34}\), and microwave irradiation\(^\text{35-38}\). Although promotion by plasma can decrease the reaction temperature, operating pressure was under atmospheric pressure. Dielectric discharge plasma can operate at atmospheric pressure and shows high conversion\(^\text{30,31}\).

The electrical field enhanced the catalytic activity even at 423 K in dry reforming. Microwave heating was attempted for dry reforming using a multi-mode or single-mode irradiation with a cuboid cavity. Many studies have found high catalytic activity under microwave irradiation\(^\text{35-38}\).

In case of the microwave heating, one problem is the reflection of microwave by active metals loaded on the support material. It has been reported, however, that the dielectric properties differ for nano-sized metal particles\(^\text{39}\).

The present study evaluated methane reforming reactions utilizing microwaves within a cylindrical cavity to assess the following: (1) The possibility of employing a supported metal catalyst in this microwave heating system; (2) Comparison of methane reforming activity between microwave heating and common heating by electric furnace; and (3) Investigating coke deposition behavior on the catalysts by microwave heating.

2. Experimental

2.1. Microwave Irradiation Apparatus

Figure 2 shows a schematic drawing of the microwave reactor, equipped with a cylindrical cavity made from aluminum, and the microwave control units. The catalyst was filled in the quartz tube and fixed along the central axis of the cavity. Microwaves were generated by a semi-conductor-type generator, which allowed precise control of both power (0-100 W) and frequency (2.3-2.7 GHz). The system automatically detected a suitable resonance frequency by feedback of information from the field detector, and tracked the optimal
microwave irradiation conditions to constantly generate a single standing wave. The surface temperature of the catalyst bed was measured by a radiation thermometer (TMHXSTM0050, Japan Sensor Corp.) using a wavelength that penetrated the quartz tube (ca. 2 μm), and the data were also sent to the microwave controller. The thermometer was calibrated using the catalyst emissivity, which was separately measured. Thermography (TH-5104, NEC Sanei Co.) was also used to measure the temperature of the catalyst bed.

Reaction gases were introduced using mass flow controllers. Vapor was introduced with a syringe pump and vaporizer. The gas line was heated by electric heater to 413 K to avoid condensation of vapor. All gases were analyzed by an online gas chromatograph (GC-2014, Shimadzu Corp.) with a thermal conductivity detector equipped with a molecular sieve 13X and a Gaskuropack 54 column (GL Sciences Inc.) for analyzing CO2, N2, H2, O2, CO, CH4, and H2O under a He carrier.

To compare microwave and conventional heating, a tubular electric furnace was also used for the reaction test. The temperature was measured with a K-type thermocouple in contact with the quartz tube. The temperatures of the tube and catalyst remained in thermal equilibrium under the reaction conditions. The temperature of the catalyst bed achieved by microwave heating was then compared with that by conventional heating.

2.2. Preparation of Catalysts

The catalyst was prepared by the incipient wetness method. γ-Al2O3 (AKP-GT00, Sumitomo Chemical Co., Ltd.) was used as a support material, and was impregnated with a palladium nitrate solution adjusted to a desired concentration, applied at loadings of 1, 5, 10, and 25 wt%. After impregnation, drying was performed at 393 K for 12 h, followed by calcination in air at 773 K for 3 h. When performing a hydrogen reduction treatment prior to the reaction, an electric furnace was used with hydrogen flow at 873 K for 1 h. The 5 wt% Ni/γ-Al2O3 catalyst was prepared using nickel nitrate as a precursor, employing the same method as for Pd/Al2O3 catalyst.

The structure of the catalysts was investigated by X-ray diffraction (SmartLab, Rigaku Corp.). The metal dispersion of the catalyst was measured by CO adsorption using a BEL-CAT chemisorption analyzer (MicromettracBEL Corp.) performed by pulsing CO into the catalyst previously reduced at 473 K under hydrogen. The catalyst after the reaction was analyzed with a thermobalance (TGA-50, Shimadzu Corp.), and the amount of deposited carbon was determined from the weight loss.

2.3. Heating Test of Catalyst and Reaction Experiments

In the reaction using the microwave heating system, 100 mg of the catalyst was filled in a quartz tube having an outer diameter of 4 mm and inner diameter of 2.4 mm. The tube was positioned coaxially in the center of the cylindrical microwave cavity.

2.3.1. Heating Ability Test

To confirm whether the prepared catalyst could be heated by microwaves, a heating experiment was attempted under N2 stream (40 mL/min). The sample was heated from 573 to 923 K at 50 K intervals, and the microwave output power was recorded.

2.3.2. Methane Reforming Reaction

Steam reforming and dry reforming of methane were performed under atmospheric pressure. The feed gas composition was 2 mL/min CH4, 6 mL/min H2O, 42 mL/min N2 for steam reforming; and 2 mL/min CH4, 2 mL/min CO2, 46 mL/min N2 for dry reforming. To investigate carbon deposition in dry reforming, the flow rate was 15 mL/min CH4, 15 mL/min CO2, 30 mL/min N2. The reaction temperature ranged from 523 K to 873 K, and the activity was compared by calculating the conversions of raw materials and the products yields.

3. Results and Discussion

3.1. Heating Ability of Supported Metal Catalysts

Dielectric heating of metallic materials by microwave irradiation is generally not possible due to the reflection of microwaves. However, it is known that heating can be performed using nano-sized particles such as a supported catalyst(9). Figure 3 shows the heating behavior of the Pd/γ-Al2O3 catalyst with the supported amount varied under an N2 gas flow. In the case of the calcined catalysts (Fig. 3(a)), the γ-Al2O3 support alone and the 1 wt% supported catalyst could not be sufficiently heated. The achieved temperature remained below the measurement limit (473 K) even when applying maximum power (100 W). In contrast, with increased Pd loading, the catalyst could be well heated in excess of 900 K at microwave power less than 40 W. After the calcination, Pd is oxidized to PdO on 5 wt% Pd/Al2O3 catalyst as suggested by the XRD spectrum (b) in Fig. 4). Since the metal oxide has relatively good dielectric properties for heating, it is considered that heating efficiency is improved with increased Pd loading under 850 K. Note that the Pd oxide decomposed to Pd metal during the heating test ((c) in Fig. 4). The structure was similar to the catalyst after hydrogen treatment ((d) in Fig. 4). Therefore, at 900 K, the heating efficiency of 5 wt% Pd/Al2O3 catalyst after calcination resembled that of catalyst after hydrogen treatment (Figs. 3(a) and 3(b)).

Under 850 K, the catalysts showed different behavior after hydrogen treatment, such that heating to 473 K or higher was not possible at either 1 % or 25 % loading (Fig. 3(b)). Although only 5 % and 10 % loadings could be heated, the efficiency of 10 % Pd was lower.
than that of the oxide, as power requiring to reach 823 K were 26 W (oxide) versus 39 W (after hydrogen treatment). The degree of metal dispersion obtained by the CO adsorption was reduced with increased loading (Table 1). That is, in the Pd metal following hydrogen treatment ((d) in Fig. 4), it is presumed that as the metal particle size increases, the microwaves are more easily reflected, thereby reducing the heating efficiency. When the supported amount is small, heating cannot be performed as in the case of oxide even if the particle size is small (Fig. 3(a)). For Pd/γ-Al2O3 catalyst, it was found that approximately 5 wt% was the optimum loading, and the reaction experiments were performed with this catalyst.

3.2. Comparison of Microwave versus Conventional Heating for Reforming of Methane

Figures 4 and 5 show the results of a reaction performed using a 5% Pd/γ-Al2O3 catalyst. In the case of steam reforming using the electric furnace heating (Fig. 5(b)) the reaction started at 600 K or higher, whereas microwave heating showed a lower reaction temperature, starting at approximately 550 K (Fig. 5(a)). This tendency is the same in dry reforming (Fig. 6). At 650 K, CO2 conversion was around 50% for microwave heating, compared with approximately 10% for conventional heating. In microwave heating, since the catalyst is heated directly, it is considered that the temperature of the catalyst layer decreases less even in the endothermic reaction. Thus, the reaction temperature is apparently decreased, as measured at the surface of the reaction bed.

The time course of the reaction at 773 K is shown in Fig. 7. The change in catalytic activity is small even after 360 min reaction (Fig. 7(a)). XRD measurements showed similar chemical state of Pd before and after the reaction as shown in Fig. 8. However, peaks of carbon were observed after the reaction ((b) in Fig. 8). The used catalysts were analyzed with a thermobalance (Fig. 9). The weight loss observed around 753 K is due to the combustion of deposited carbon. We previously reported that carbon deposition can be detected by the shift of resonance frequency during single-mode microwave irradiation. The shift of microwave frequency during the reaction from 2457 to 2450 Hz (Fig. 7(b)) suggested both carbon deposition and efficiency of microwave absorption.

Note that stable reaction was maintained by appropriate feedback control of the microwave output and frequency (Fig. 7(b)). These feedback control of both power and frequency maintained the standing wave even if changes in electrical property occurred in the
catalyst.

3.3. Restriction of Carbon Deposition on Ni/γ-Al2O3 Catalyst

One problem encountered in dry reforming of methane is the deposition of coke materials. To determine the effects of microwave heating on carbon deposition, the reaction was performed at 803 K for 7 h using a 5 wt% Ni/γ-Al2O3 catalyst by microwave heating and conventional heating. After the reaction, the catalysts were analyzed with a thermobalance (Fig. 10). The catalyst showed less weight loss after microwave heating and the deposition of coke material was suppressed compared with the common method of electric furnace heating. As suggested in the previous chapter, deposited carbon is a good microwave absorber, thus causing local heating35),36),41). Therefore, the reaction under the microwave irradiation provided suitable conditions for carbon combustion resulting in stable catalytic activity.

4. Conclusion

Methane reforming was performed using heating with microwave radiation in a cylindrical cavity reactor. After confirming the ability to heat supported metal catalysts by microwave radiation, the reaction characteristics were compared between microwave and conventional heating methods. The main conclusions are as follows.

When Pd was in the form PdO, the heating efficiency
of the Pd/γ-Al2O3 catalyst was improved with increased loading amount. After hydrogen reduction, appropriate metal loadings were found to be 5 to 10 wt% by weight. At more than 10 wt% catalyst loading, heating efficiency was reduced due to reflection of the microwaves.

Conversion of methane by both steam reforming and dry reforming was higher using microwave heating than using conventional heating. The catalyst was directly heated by dielectric heating, so preventing temperature decrease in the catalyst bed by the endothermic reaction.

Microwave heating suppressed coke deposition over Ni/γ-Al2O3 catalyst as compared to conventional heating, and showed effective restriction of carbon deposition on the catalyst.

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要  旨
円筒状キャビテを用いたシングルモードマイクロ波照射加熱によるメタンの改質反応

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固体触媒を用いた流通式反応にマイクロ波照射加熱を利用したため，メタンの改質反応を円筒型の照射空間を備えたシステムで行った。円筒型照射空間内では定在波が形成され，常に中心部で電界強度が最大となるため，そこに設置した反応管に均一にマイクロ波が照射される。マイクロ波加熱効率が良好な5 wt% Pd/Al2O3触媒を用いた反応では，水蒸気改質とドライフォーミングのどちらもマイクロ波加熱が電気炉加熱より高い転化率を示した。また，マイクロ波加熱では炭素質の析出も抑制されることがNi/Al2O3触媒を用いた反応で分かった。これらは，マイクロ波加熱では触媒が直接誘電加熱されるため，反応管内部まで十分に熱が供給されることに起因しているものと考えられ，本システムが固体触媒を用いた流通式反応に効果的であることが示された。

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