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Production of pure hydrogen from methane by low temperature plasma processing

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Abstract−Production of pure hydrogen from methane by a low temperature plasma process coupled with catalytic reaction was investigated. In low temperature plasma, methane molecules were converted to thin solid films and hydrogen. The conversion of methane and the hydrogen yield depended on the flow rate of methane and the discharge power for the low temperature plasma process. They increased as the flow rate decreased and the discharge power increased. A conversion as high as 87.4% and hydrogen yield as high as 67% could be obtained, but the purity of the hydrogen was less than 90%. The purity could be increased to 100% by coupling the low temperature plasma process with a catalytic reaction using a plasma-catalyst hybrid system.

Keywords: Production of Pure Hydrogen, Methane, Low Temperature Plasma, Plasma-catalyst Hybrid System

INTRODUCTION

Hydrogen is drawing attention as an alternative energy source for fossil fuels because of its high efficiency, abundance, and cleanness. It can be produced from primary energy sources such as water, alcohols, biomass, and natural gas. Although there are many kinds of processes to produce hydrogen [1-9], steam-reforming of natural gas has been known to be the most efficient and widely used for decades. However, the process has a drawback of large consumption of energy and emitting of CO_2. As a consequence, efforts have been given to the development of a green technology to replace the steam-reforming process and they are focused on the application of a plasma process.

Early on, the plasma process was investigated mainly for the gasification of fossil fuels [10]. Recently, however, its applications for the various reforming processes and the production of hydrogen have been intensively investigated [11-17]. It has been claimed that the plasma process shows high conversion efficiency and hydrogen selectivity [11,12], especially when the plasma process is combined with a catalytic reaction [13-15]. However, production of pure hydrogen from hydrocarbons has not been reported yet.

In this study, we investigated the production of pure hydrogen from methane by a low temperature plasma process coupled with catalytic reaction using a plasma-catalyst hybrid system. In low temperature plasma, methane molecules can easily decompose and produce carbon and hydrogen radicals. The produced radicals can recombine to form C-C, C-H, or H-H bonds. If the recombination between carbon radicals repeatedly occurs consecutively, they grow as a polymer and deposit on surfaces of solid materials such as electrodes and a reactor wall [18,19]. As a result, most of the carbons in the methane molecules can be eliminated in the form of thin solid films. Hydrogen radicals that form C-H bonds have high possibility to incorporate into the growing films, but those that form H-H bonds result in the production of hydrogen.

Since, the degree of decomposition can depend on the operating parameters such as discharge power and flow rate of methane, their effects on the production rate of hydrogen were investigated by varying conditions of the operating parameters. And, not all of carbons in methane molecules were expected to be eliminated by the low temperature plasma process alone; catalytic reaction was coupled with the low temperature plasma process for further elimination of the residual methane molecules.

EXPERIMENTS

The plasma-catalyst hybrid system used for this study, shown in

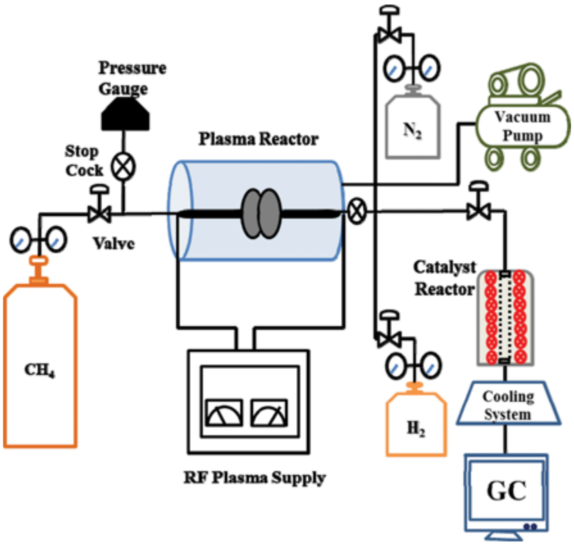

Fig. 1. Schematic diagram of the plasma-catalyst hybrid system.

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Fig. 1, consists of a tubular plasma reactor (inner diameter of 14.2 cm and length of 28 cm) and a catalyst reactor (inner diameter of 1.27 cm and length of 40 cm). Hot and ground electrodes (stainless steel discs with diameter of 8.0 cm) are located in the middle of the reactor and connected to an R.F. (13.56 MHz) power supply (Auto Electric Company, R600A with an Automatic Matching Net Work LC 1000S). Distance between the electrodes is 2.5 cm. The system was evacuated to 2.4×10^{-3} Torr, and methane (Daechang Gas Inc., 99.95%) was allowed to flow to the plasma reactor. Electric discharge power was supplied to create low temperature plasma when the pressure in the reactor was stabilized. Flow rates of methane ranged between 10 and 30 SCCM. Discharge powers ranged between 100 and 600 W. For the catalytic reaction, 5 g of Ni/Al_2O_3 commercial catalysts (Süd-chemie Catalyst Inc., FCR-4) were filled in the catalyst reactor. Temperature of the reaction ranged between 400 and 700 °C. The catalysts were reduced at 700 °C for 1 hour in a hydrogen flow of 10 SCCM and a nitrogen flow of 10 SCCM before every batch of the reaction.

A gas chromatograph equipped with a thermal conductivity detector (Yunglin Instrument, M600D) was used for the analysis of effluent gas. A Molecular Sieve 5A column (Supelco 60/80) was used for the detection of hydrogen and a Hyesep Q column (Supelco 80/100) was used for the detection of hydrocarbons. An FT-IR/ATR spectrometer (Shimadzu, IRPrestige-21) was used for the analysis of chemical structure of the deposited thin solid films. An EDX spectrometer (Horiba, EX-250) was used for the detection of carbon deposits in the catalysts after the catalytic reaction.

RESULTS AND DISCUSSION

The low temperature plasma process converted methane molecules to thin solid films and hydrogen. The thin solid films were found to be deposited on the surfaces of electrodes and inner wall of the plasma reactor. The deposition of thin films supports that methane molecules were solidified through plasma polymerization. Methane and hydrogen were detected in effluent gas. No other kinds of hydrocarbons were detected in the effluent gas, which indicates that all the carbons in the decomposed products of methane were eliminated through the solidification by plasma polymerization [19]. Flow rates of the detected methane and hydrogen in the effluent gas were determined based on their GC peak areas and used for the calculation of conversion of methane (%) and hydrogen yields (%) as follows:

Conversion of Methane

$$=\frac{\text{flow rate of methane in feed}-\text{flow rate of methane in effluent gas}}{\text{flow rate of methane in feed}}\times100 \tag{1}$$

$$\text{Hydrogen Yield}=\frac{\text{flow rate of hydrogen in effluent gat}}{2\times\text{flow rate of methane in feed}}\times100 \tag{2}$$

The low temperature plasma process is quite effective for the conversion of methane and the production of hydrogen. Conversions of methane up to 87.4% and hydrogen yields up to 67% were obtained depending on operating conditions of the low temperature plasma process. The conversion of methane depended on the discharge power (W) and the flow rate of methane (F). Fig. 2 shows the conversion of methane as a function of discharge power for various flow rates of methane. They increase as the discharge power increases and the flow rate decreases, which indicates that they have a close relationship with the supplied energy per mole of methane (W/F). Fig. 3 shows conversions of methane as a function of W/F. Three curves for three different flow rates of methane in Fig. 2 are getting closer and start to increase linearly as the W/F increases in the beginning but become saturated as the W/F further increases, which implies that most of the supplied energy is consumed for the decomposition of methane molecules when the W/F is low but not when the W/F is high. The supplied energy is believed to be transferred mainly by collisions of energetic species created in the low temperature plasma. The collisions of energetic species are expected to be dominant with methane molecules when the W/F is low since most of methane molecules are not yet decomposed, but the collisions are expected to be dominant with decomposed products of methane when the W/F is high. Therefore, it seems to be difficult

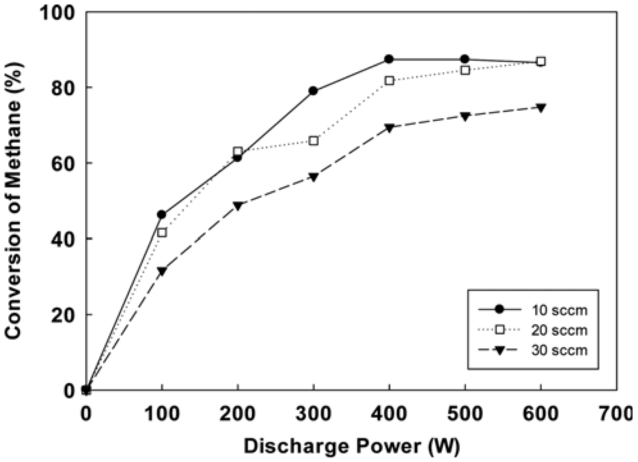

Fig. 2. Conversions of methane by low temperature plasma process as a function of discharge power for various flow rates of methane.

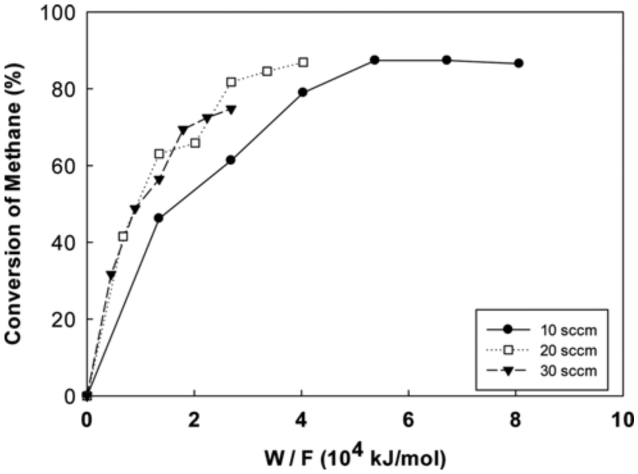

Fig. 3. Conversions of methane by low temperature plasma process as a function of W/F.

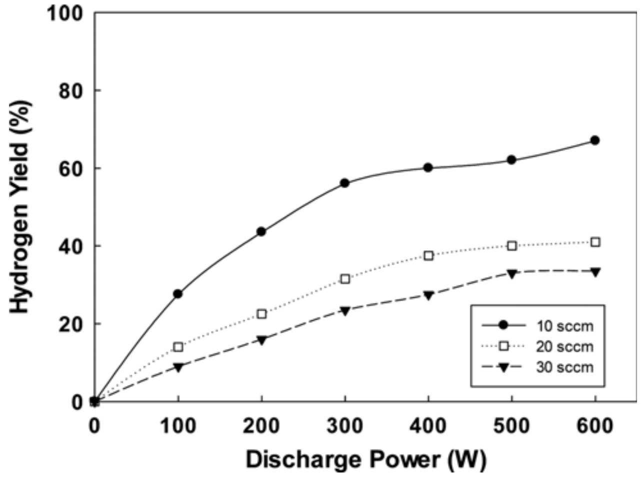

Fig. 4. Hydrogen yields by low temperature plasma process as a function of discharge power for various flow rates of methane.

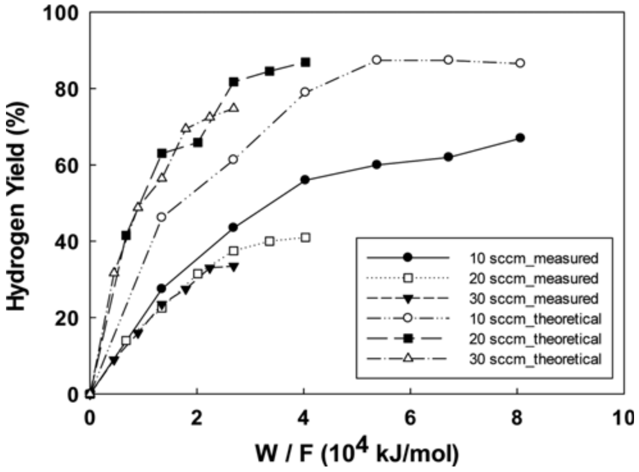

Fig. 5. Measured and theoretical hydrogen yields by low temperature plasma process as a function of W/F.

to convert all methane molecules to pure hydrogen by the low temperature plasma process alone due to the decreasing energy-efficiency of the process as the W/F increases. The lower conversion at 10 SCCM than that at 20 and 30 SCCM for the same W/F may be explained by lower probability of the collisions at lower flow rate of methane.

The increase of the conversion of methane resulted in the increase of the hydrogen yield. Fig. 4 shows the hydrogen yields as a function of discharge power for various flow rates. They also increase as the discharge power increases and the flow rate decreases, showing a similar pattern to that of the conversions of methane. However, they were lower than theoretically expected values from the conversions of methane in Fig. 2 for all conditions of the process. Since only hydrogen and methane were detected in the effluent gas, the measured values should be identical with the theoretical values if all hydrogen atoms in methane molecules are converted to hydrogen molecules. The differences between the theoretical values and the measured values for the same W/F are clearly seen in Fig. 5. The lower hydrogen yields than the theoretical values seem to be due to loss of some hydrogen atoms by their incorporation into the deposited thin solid films. In the low temperature plasma process, hydrogen radicals or hydrocarbon radicals generated by the decomposition of methane molecules can be incorporated into the growing deposited films through the recombination with carbon radicals in the films. Fig. 6 shows FT-IR/ATR spectra of the deposited thin solid films on the stainless-steel disc located on the wall in the middle of the reactor at various discharge powers and flow rates of methane. C-H stretching bands are shown in the spectra in the region between 2,800-3,000 cm^{-1}, which indicates that the deposited thin solid films are hydrocarbon films. And, peak intensity of the band gets larger as discharge power decreases and flow rate of methane increases. Therefore, the effect of the loss on the lowering of hydrogen yield is expected to be more pronounced when the low temperature plasma process is carried out at low discharge power and high flow rate of methane, and thus at low W/F. This is well represented in Fig. 5. The hydrogen yield at the lowest

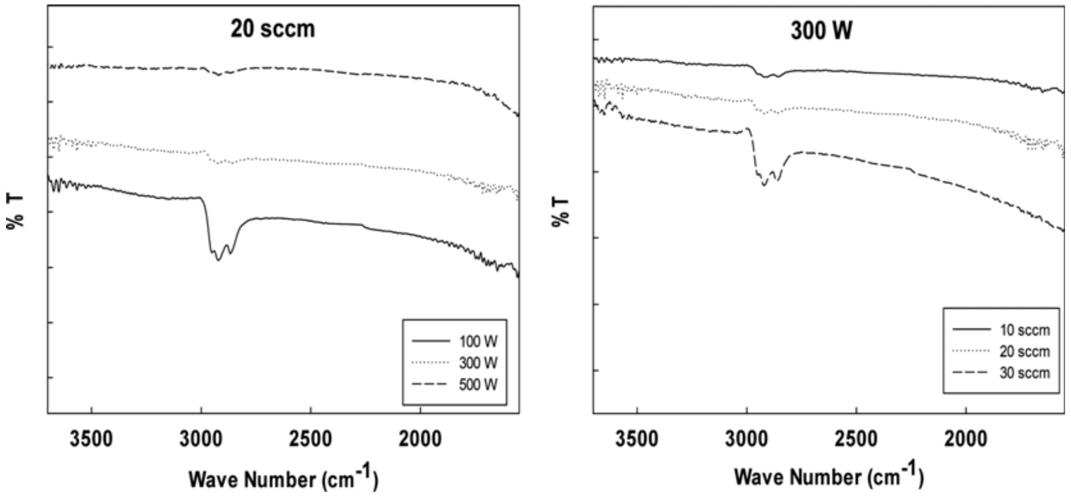

Fig. 6. FT-IR/ATR spectra of thin solid films deposited by low temperature plasma process at various discharge powers and flow rates of methane.

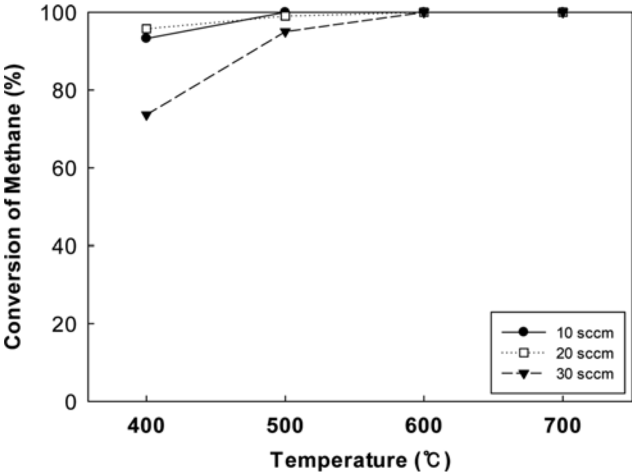

Fig. 7. Conversions of methane by catalytic reactions at various temperatures.

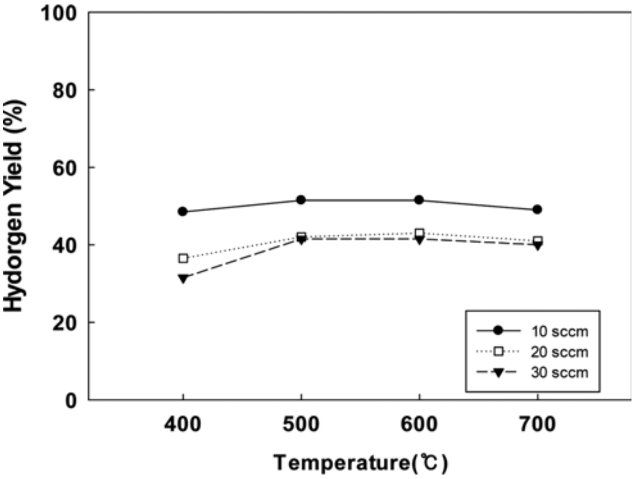

Fig. 8. Hydrogen yields by catalytic reactions at various temperatures.

W/F (0.45×10^4 kJ/mol; 100 W, 30 SCCM) is only 28.6% of the theoretical value, while hydrogen yield at the highest W/F (8.06×10^4 kJ/mol; 600 W, 10 SCCM) is 76.7% of the theoretical value. And, it is also seen that hydrogen yields at 10 SCCM are higher than those at 20 and 30 SCCM for the same W/F on the contrary to the conversions in Fig. 3.

The catalytic reaction with Ni/Al_2O_3 catalysts was more effective than the low temperature plasma process to obtain high conversions of methane but not to obtain high hydrogen yields. As shown in Fig. 7 and 8, a conversion as high as 100% could be obtained if the reaction temperature is higher than 600 °C but the highest hydrogen yield is at the most 50%. Therefore, the low temperature plasma process was coupled with the catalytic reaction using a plasma-catalyst hybrid system to investigate the effect. Two kinds of effect were obtained. One was that pure hydrogen could be produced independently of the flow rate of methane and the discharge power

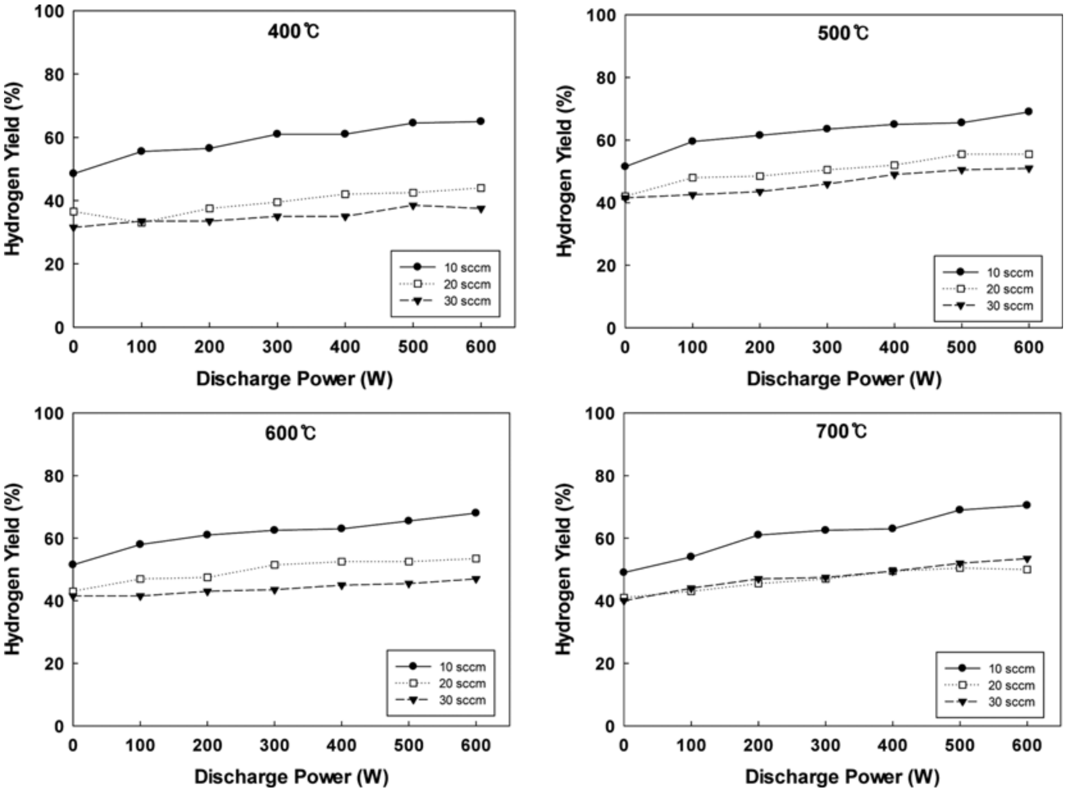

Fig. 9. Hydrogen yields by low temperature plasma process and catalytic reaction as a function of discharge power for various flow rates at various temperatures of catalytic reaction.

for all temperatures of the catalytic reaction between 400-700 °C. In effluent gas, only hydrogen was detected, because a part of methane molecules are eliminated through solidification in the low temperature plasma process before they enter into the catalytic reactor. The other was that hydrogen yields could be increased even at low discharge powers and high flow rates of methane. Fig. 9 shows the hydrogen yields as a function of discharge power for various flow rates of methane and temperatures of catalytic reaction. They are higher than the hydrogen yields obtained by the low temperature plasma process alone or by the catalytic reaction alone and less dependent on the discharge power. In addition to those effects, the coupled reaction has an advantageous aspect in that the life-time of the catalysts can be prolonged. Since most of the carbons are eliminated through the solidification by plasma polymerization, deactivation of the catalysts by coking can be reduced. When catalysts were analyzed by EDX after 60 hours, the amount of carbon deposits in the catalysts used for the coupled reaction (400 W, 30 SCCM, 700 °C) was measured to be only 0.13 weight%, while the amount of carbon deposits in the catalysts used for the catalytic reaction alone (30 SCCM, 700 °C) was measured to be 1.82 weight%.

CONCLUSIONS

A low temperature plasma process is suitable for the production of hydrogen from methane, but pure hydrogen is difficult to produce. Conversion of methane as high as 87.4% can be obtained with the hydrogen yield as high as 67%. Catalytic reaction with Ni/Al_2O_3 catalysts is a suitable process for the production of pure hydrogen, but high hydrogen yield is difficult to obtain. If the low temperature plasma process is coupled with the catalytic reaction, however, pure hydrogen can be produced with high hydrogen yield, and the life-time of the catalysts can be prolonged due to reduced coking.

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