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Small Reformer for Steam Reforming of Methanol Using Ni Nanoparticles on a Ceramic Surface

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A small reformer for steam reforming of methanol was produced using an $Mg_{2/3}Ni_{1/3}O$ ceramic catalyst that was reduced by hydrogen. In the catalyst, small nickel particles were dispersed on the ceramic surface. The reformer consists of a fuel vaporizer, a steam reformer, and two CO removers. These are covered with heat shield materials and a stainless steel case with overall dimensions of 260 mm (length) × 60 mm (width) × 25 mm (thickness). The reforming temperature can be controlled up to a level of 500℃ by a ceramic heater built into the reformer. This system could reform $H_2O:CH_3OH=4:1$ (molar ratio) fuel into hydrogen-enriched gas at 400℃ and could supply about 100 cc/min of hydrogen-enriched gas. A conventional fuel cell could successfully supply electricity using the gas produced by the reformer.

Key words: Catalyst, steam reforming, reformer, hydrogen, fuel cell

1. INTRODUCTION

It is important to use the limited hydrocarbon fuel sources on earth efficiently. Natural gas, containing mainly methane (CH_4), is a valuable energy source. Given the need for stable energy supplies, the conversion of methane to a versatile feedstock has attracted increasing interest. However, CH_4 is not suitable for mobile electric systems because it can only be carried in high- pressure gas cylinders, which are heavy.

Methanol is one of the most promising fuels for producing hydrogen for polymer electrolyte fuel cells (PEFCs) because of its high hydrogen to carbon ratio (4:1), low reforming temperature, and low cost. Steam reforming of methanol has been commonly demonstrated using Ni-based catalysts [1-3] and exhibits high selectivity of H_2 and CO_2 at relatively low temperatures (300℃-400℃). The operating conditions in PEFC systems are severe, with the CO concentrations of more 100 ppm in the gases causing great deterioration of cell performance [4]. Therefore, it is necessary to develop a reformer with long-term stability that produces almost CO-free hydrogen. On the other hand, the size of the reformer is also important.

The small reformer for the steam reforming of methanol produced in this study uses Ni-based catalyst and could supply about 100 cc/min hydrogen-enriched gas, which could successfully be used by a conventional fuel cell to supply electricity.

2. EXPERIMENTAL METHOD

MgO (010298, Kojundo Chemical Laboratory Co., Ltd., Japan) and NiO (FP10367, Sumitomo Metal Mining Co., Ltd., Japan) powders were used as the starting materials for fabricating the ceramic Ni-based catalyst. The 1.0NiO/2.0MgO molar ratio powder (a solid solution of (Ni, Mg)O was formed in this composition) was mixed with ethanol using a ball mill. After removing the ethanol, extrusion molding was conducted with 10% binder to produce a plate ceramic precursor of the catalyst. This precursor was sintered at 1300℃ for 5 hours and was reduced by hydrogen (500 cc/min) at 1000℃ for 10 min. The microstructures were examined by scanning electron microscopy (SEM).

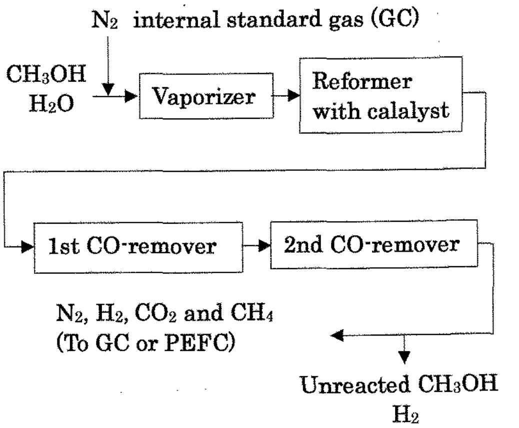

Fig. 1 Schematic drawing of the reforming system.

The reforming activity of the fabricated catalyst was investigated in the system shown in Fig. 1. The system was made of stainless steel. The vaporizer was heated to 150℃, and the fuel, an aqueous solution of methanol, was introduced into the vaporizer by an automatic syringe. The reformer and the CO-removers were controlled at 400℃and 200℃-300℃, respectively. The molar ratio of the steam/methanol fed to the catalyst was 4/1, and the total flow rate of the feed gas was 150 cc/min. The concentrations of H_2, CO, CO_2, and CH_4 in the exhaust gas were analyzed by gas chromatography

(GC) with a thermal conductivity detector (He, 100℃) and a Molsieve 5-Å column (Ar, 100℃). Nitrogen was introduced as an internal standard gas before entry into the gas chromatograph. The flux of the H_2 gas output was measured by a flow meter. Finally, a conventional PEFC (H-TEC PEMFC kit) was run using the reformed gas.

3. RESULTS AND DISCUSSION

The structure of the fabricated precursor of the monolithic catalyst with dimensions of 21 mm × 40 mm × 1 mm can be seen in Fig. 2. The figure shows 3 plates of the ceramic catalyst after dicing.

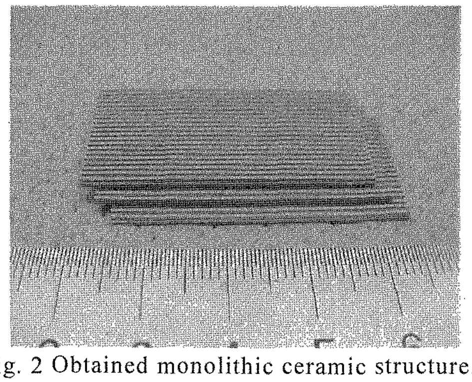

Fig. 2 Obtained monolithic ceramic structure.

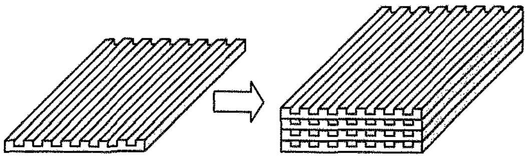

Fig. 3 Pseudo-honeycomb structure of the calalyst for the reformer.

Figure 3 shows a pseudo-honeycomb structure made from 3 layers of catalyst plates. After partial reduction, the pseudo-honeycomb is placed in a stainless steel case to fabricate the reformer shown in Fig. 4. The fuel gas passes though the numerous canals in this structure and is reformed to H_2, CH_4, CO_2, and CO.

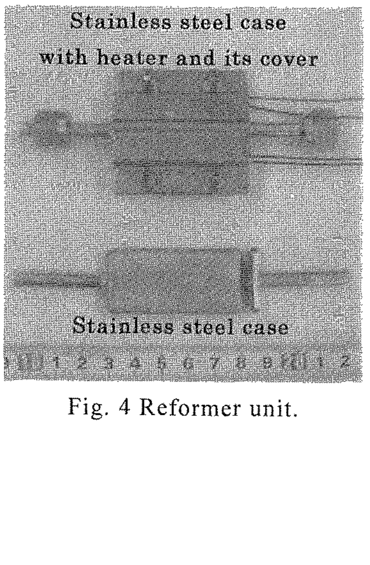

Fig. 4 Reformer unit.

The microstructure of the canal surface of the pseudo-honeycomb Ni/MgO catalyst as observed by SEM is shown in Fig. 5. The nanoparticle deposits seen in the image are mainly Ni particles on MgO ceramic.

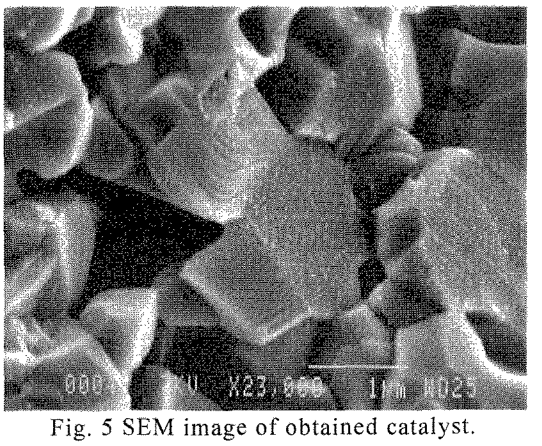

Fig. 5 SEM image of obtained catalyst.

A ceramic heater was built into the reformer unit. The reformer unit was connected to a vaporizer and two CO-removers in a 260 mm × 60 mm × 25 mm case with thermal insulation wool as shown in Fig. 6 to produce the small reformer system used in this study. The reforming performance of this system is shown in Table I. The CO concentration in the obtained gas is below the detection limit; therefore, this reforming system is suitable for PEFC. However, the H_2 concentration is slightly less than that obtained by reforming with a conventional Pt catalyst (about 70%). We will try and raise the obtained H_2 concentration by using another base metal in the near future.

Table I Performance of the reforming system

Operation temperature (℃)	400
Concentration of H_2 (%)	65.8
Concentration of CO (ppm)	Below the detection limit
Total H_2 flow rate (cc/min)	>100

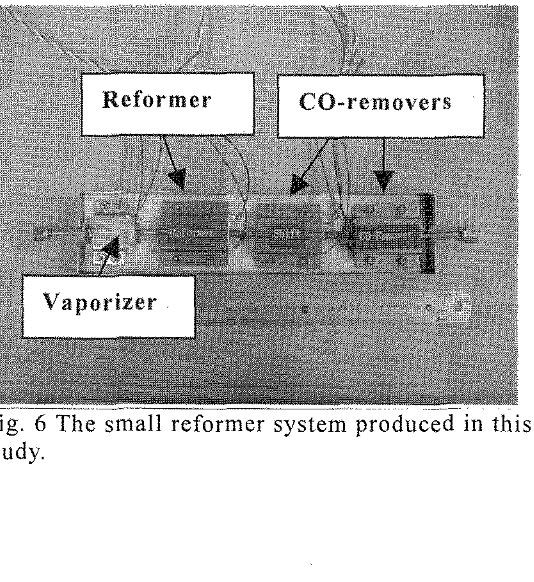

Fig. 6 The small reformer system produced in this study.

Finally, the small reformer was connected to a PEFC and fuel was passed through the system as shown Fig. 7. The system could successfully supply electricity and turn the propeller continuously. Thus a composite partially reduced catalyst of a base metal such as Ni and ceramic was found to be suitable for use in reformers.

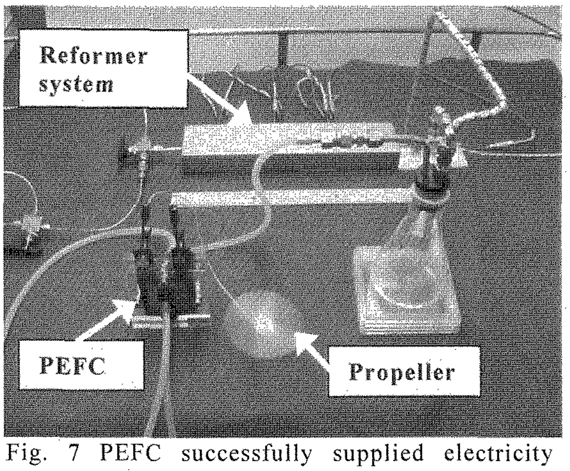

Fig. 7 PEFC successfully supplied electricity using the gas from the reforming system

SUMMARY

A small reformer for steam reforming of methanol was produced using an $Mg_{2/3}Ni_{1/3}O$ ceramic catalyst that was reduced by hydrogen. The size of this reformer is 260 mm×60 mm×25 mm. This system reformed the H_2O:CH_3OH= 4:1(molar ratio) fuel into hydrogen-enriched gas at 400℃. The main results of our experiments are as follows:

1) The reformer supplied more than 100 cc/min of hydrogen-enriched gas.
2) There is almost no CO in the reformed gas produced by this reformer.
3) Using the gas provided by this reformer, a conventional PEFC could successfully supply electricity.
4) A composite partially reduced catalyst of a base metal such as Ni and ceramic was found to be suitable for use in reformers.

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