

## 니켈계 촉매상에서 메탄에 의한 이산화탄소의 개질 반응

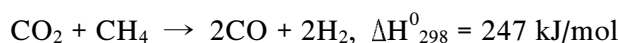
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### CO<sub>2</sub> reforming by CH<sub>4</sub> over Ni-based catalysts

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#### Introduction

Carbon dioxide (CO<sub>2</sub>) is a greenhouse effect gas and contributes much to global warming, the reduction and sequestration of CO<sub>2</sub> has been attracting interest from an environmental perspective.



The reaction has an advantage of the production of synthesis gas as well as the reduction of greenhouse gas. It is of special interest from an industrial perspective since it produces a synthesis gas with a low H<sub>2</sub> / CO ratio, which can be preferentially used for Fischer-Tropsch synthesis [1]. But the CO<sub>2</sub> reforming by CH<sub>4</sub> has two serious problems. The reaction is an intensively endothermic reaction, which consumes much energy and the other is carbon formation on surface of catalyst used in the reforming.

During the past decades, much effort has been focused on the development of catalyst which show high activity and stability against coking for long-term operation. Numerous metal catalysts were studied for this reaction. Among them, nickel-based catalysts [3] and noble metal catalysts [4] have been showing the promising catalytic performance in terms of activity and selectivity to synthesis gas. Noble metal catalysts have been found to have resistance against coking. But it does not seem to be practical because of the high cost of the noble metals. To solve these problems, author suggested an electrocatalytic internal reforming of CO<sub>2</sub> by CH<sub>4</sub> to coproduce a syngas and an electricity in a solid oxide fuel cell (SOFC) system [5-7].

In this work, we have studied the CO<sub>2</sub> reforming by CH<sub>4</sub> over Ni-YSZ-CeO<sub>2</sub> and Ni-YSZ-MgO catalysts to check the possibility for the development of a high performance catalyst electrode for application in an electrocatalytic reforming in the SOFC system.

#### Experimental

The catalyst material was a mixture of NiO and YSZ (NiO : YSZ = 35 : 65 vol%). NiO powder (99.99%, Sigma-Aldrich Co.) has a diameter ca. 6.2 μm, and YSZ powder (TZ-8Y, TOSOH Co.) consisted of ZrO<sub>2</sub> doped with 8 mol% Y<sub>2</sub>O<sub>3</sub>. The CeO<sub>2</sub> (99.9%, Sigma-Aldrich Co.) or MgO (98%, Nakarai Chemical Co.) powder was added to the mixture. The sample was pulverized into powder by a ball mill.

The carbon dioxide reforming by  $\text{CH}_4$  was carried out in a conventional fixed bed reactor system (Fig.1). Flow rates of reactants were controlled by mass flow controllers [Bronkhorst HI-TEC Co.]. The quartz reactor with an inner diameter of 7 mm was heated in an electric furnace. The reaction temperature was controlled by a PID temperature controller and was monitored by a separated thermocouple placed in the catalyst bed. The product gases were analyzed by an on-line GC equipped with a thermal conductivity detector (TCD) and a carbosphere column.

BET surface area and total pore volume of the prepared catalysts were measured by  $\text{N}_2$  physisorption using a sorption analyzer [Quantachrome Co., Autosorb-1C]. Structure of the catalysts was analysed by a XRD analyzer [Shimadzu Co., XRD-6000].

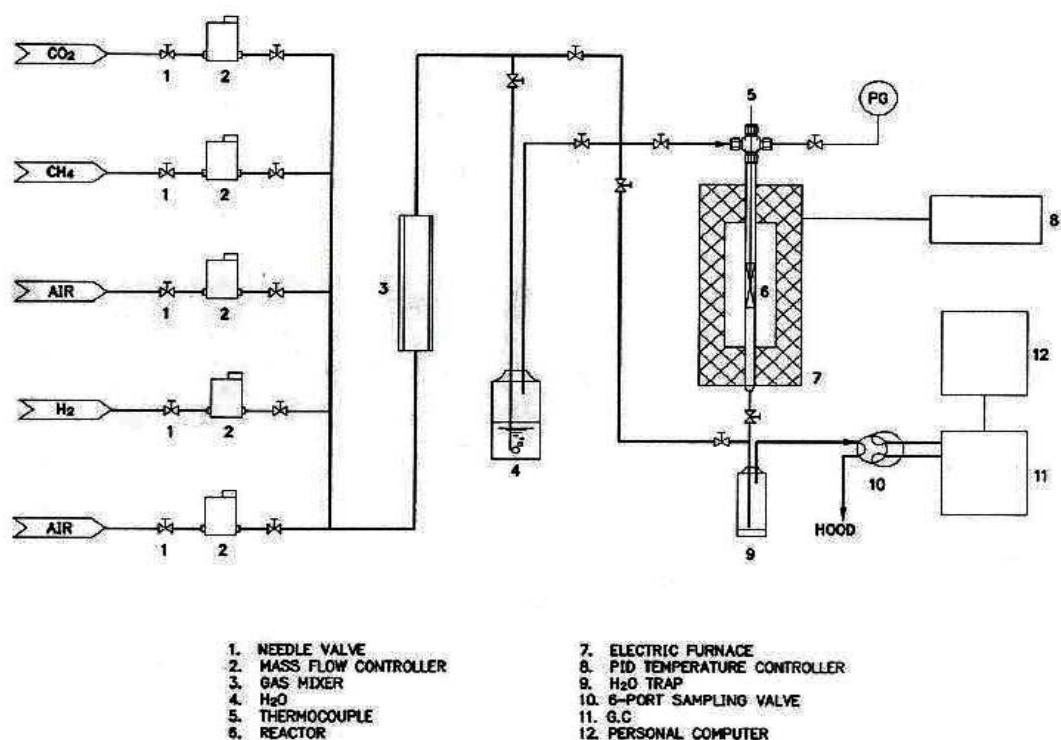


Figure. 1. Schematic diagram of the fixed reactor system

## Results and Discussion

The BET surface area and total pore volume of the prepared catalysts before and after the reaction were summarized in Table 1. BET surface area and total pore volume of the Ni-YSZ- $\text{CeO}_2$  and Ni-YSZ- $\text{MgO}$  catalysts after the reaction increased 54%, 75% and 51%, 67%, respectively. It was identified that BET surface area of the catalysts increased by the formation of carbon. The change of the surface area of active metal will be discussed after measuring CO Chemisorption for the catalyst before and after the reaction.

Table 1. The BET surface area and total pore volume of Ni-YSZ-CeO<sub>2</sub> and Ni-YSZ-MgO catalysts before and after the reaction.

| Catalyst                |                 | BET surface area (m <sup>2</sup> /g) | Total pore volume (cc/g) |
|-------------------------|-----------------|--------------------------------------|--------------------------|
| Ni-YSZ-CeO <sub>2</sub> | before reaction | 10.2                                 | 0.004                    |
|                         | after reaction  | 15.7                                 | 0.007                    |
| Ni-YSZ-MgO              | before reaction | 8.9                                  | 0.003                    |
|                         | after reaction  | 13.4                                 | 0.005                    |

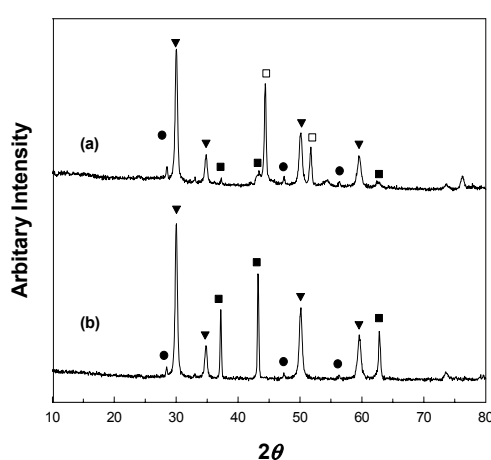


Fig 2. XRD patterns of Ni-YSZ-CeO<sub>2</sub> catalyst before and after the catalytic reforming of CO<sub>2</sub> by CH<sub>4</sub>. ■: NiO, □: NiC ▼: YSZ, ●: CeO<sub>2</sub>  
(a) after reaction (b) before reaction

The conversions of CO<sub>2</sub> and CH<sub>4</sub> over Ni-YSZ-CeO<sub>2</sub> catalyst were obtained 86% and 80%, respectively. Figure 4 shows the effect of reaction temperature on the conversions of CO<sub>2</sub> and CH<sub>4</sub> over the prepared catalysts. It was found that the Ni-YSZ-CeO<sub>2</sub> catalyst showed higher activity than the Ni-YSZ-MgO catalyst at temperature range of 650 ~ 850 °C, and the maximum activity was observed at above 800 °C. The H<sub>2</sub> and CO produced in the catalytic reforming can be applied as fuel gas in the SOFC system. Because the electrochemical reactions are generally proceeded between 700 °C and 900 °C to produce the electricity when H<sub>2</sub> was used as a reactant in the SOFC system, it was considered that the Ni-YSZ-CeO<sub>2</sub> catalyst can be applied as an anode catalyst to coproduce the syngas and the electricity in the SOFC system. The syngas released from the anode side can be applied as a raw material for the production of high-valued chemicals.

It was concluded that the Ni-YSZ-CeO<sub>2</sub> catalyst is a promising candidate for development as a catalyst anode material for an electrocatalytic reforming in the SOFC system.

Figure 2 represents the X-ray diffraction (XRD) patterns of the Ni-YSZ-CeO<sub>2</sub> catalyst before and after the reaction. It is found that NiO changed into NiC after reaction for 50 h. In spite of the fact that a significant amount of carbon was formed during the reaction over Ni-YSZ-CeO<sub>2</sub>, the catalyst exhibited high stability for 50 h.

Figure 3 shows the conversions of CO<sub>2</sub> and CH<sub>4</sub> over Ni-YSZ-CeO<sub>2</sub> and Ni-YSZ-MgO catalysts with a time on stream. The catalytic reforming reaction of a mixture of CO<sub>2</sub> (12 vol%) and CH<sub>4</sub> (12 vol%) was carried out at the reaction conditions of 800 °C, atmospheric pressure and total flow rate of 20 cc/min for 50 h. It was found that Ni-YSZ-CeO<sub>2</sub> catalyst presented higher activity than Ni-YSZ-MgO catalyst under the tested conditions. The

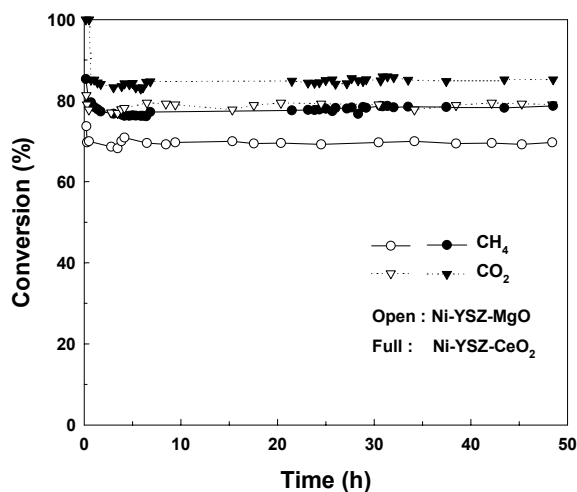


Figure 3. The conversion of CO<sub>2</sub> and CH<sub>4</sub> over Ni-YSZ-CeO<sub>2</sub> and Ni-YSZ-MgO catalysts with a time on stream at 800°C.

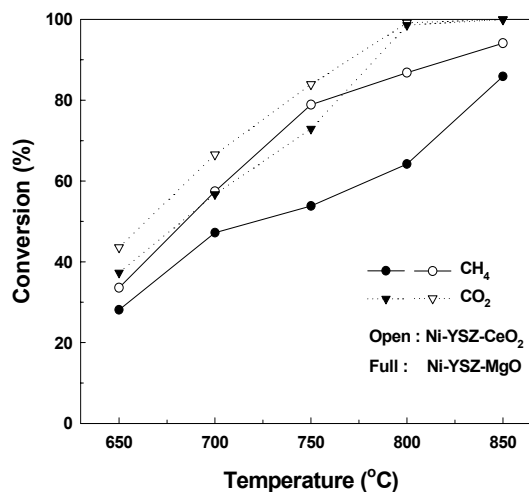


Figure 4. The effect of reaction temperature on the conversions of CO<sub>2</sub> and CH<sub>4</sub> over Ni-YSZ-CeO<sub>2</sub> and Ni-YSZ-MgO catalysts.

### Acknowledgement

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