

Ni-YSZ-CeO₂ 촉매상에서 메탄에 의한 이산화탄소의 개질 반응

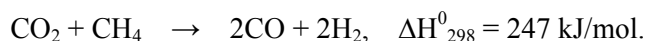
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Carbon Dioxide Reforming by Methane over Ni-YSZ-CeO₂ Catalyst

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Introduction

Carbon dioxide (CO₂) is a greenhouse effect gas and contributes much to global warming, the reduction and sequestration of CO₂ has been attracting interest from an environmental perspective. The CO₂ reforming by CH₄ is one of the CO₂ conversion methods:



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 synthesis gas with a low H₂ / CO ratio, which can be preferentially used for Fischer-Tropsch synthesis [1-2]. Furthermore, both CH₄ and CO₂ are the cheapest reactants and most abundant carbon-containing materials. However, the CO₂ reforming by CH₄ is a highly energy consuming and coke forming process. To solve these problems, author suggested an electrocatalytic internal reforming of CO₂ by CH₄ to coproduce a syngas and an electricity in a solid oxide fuel cell (SOFC) system [3-6].

In this work, we have studied the CO₂ reforming by CH₄ over Ni-YSZ-CeO₂ and Ni-YSZ-MgO catalysts to check the possibility of development of a high performance catalyst electrode for application in an electrocatalytic reforming in the SOFC system.

Experimental

The catalyst was prepared by a physical mixing of NiO and YSZ powders (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 ZrO₂ doped with 8 mol% Y₂O₃. The CeO₂ (99.9%, Sigma-Aldrich Co.) or MgO (98%, Nakarai Chemical Co.) powder was added to the mixture. The sample was pulverized into powder by an attrition mill.

The carbon dioxide reforming by CH₄ 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, total pore volume and active metal surface area of the prepared catalyst were measured by using a sorption analyzer [Quantachrome Co., Autosorb-1C]. Structure of the catalyst was analysed by a XRD analyzer [Shimadzu Co., XRD-6000].

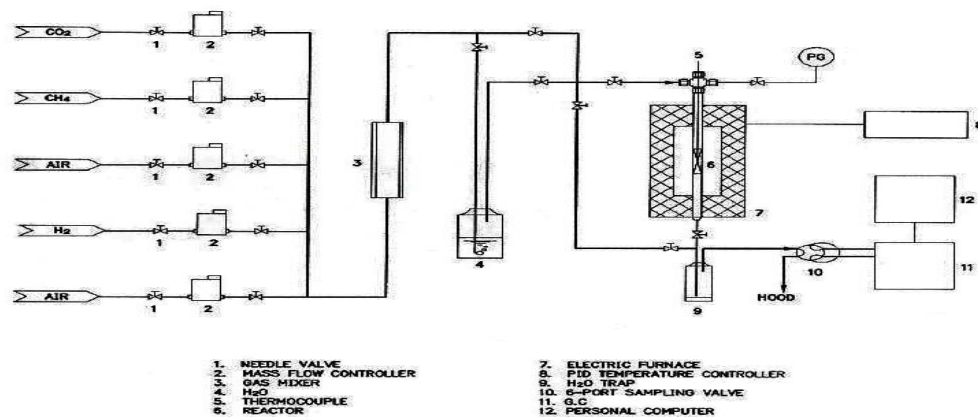


Fig. 1. Schematic diagram of the fixed reactor system.

Results and discussion

In order to investigate the catalytic activity of prepared catalysts, CO₂ reforming by CH₄ was carried out in the fixed bed reactor system. Figure 2 shows the conversion of CO₂ and CH₄ over Ni-YSZ-CeO₂ and Ni-YSZ-MgO catalysts with a time on stream. The catalytic reforming reaction of a mixture of CO₂ (12 vol%) and CH₄ (12 vol%) was carried out at the reaction conditions of 800 °C, atmosphere and total flow rate of 20 cc/min. It was found that Ni-YSZ-CeO₂ catalyst presented higher activity than Ni-YSZ-MgO catalyst under the tested conditions. The conversions of CO₂ and CH₄ over Ni-YSZ-CeO₂ catalyst were obtained 86% and 80%, respectively.

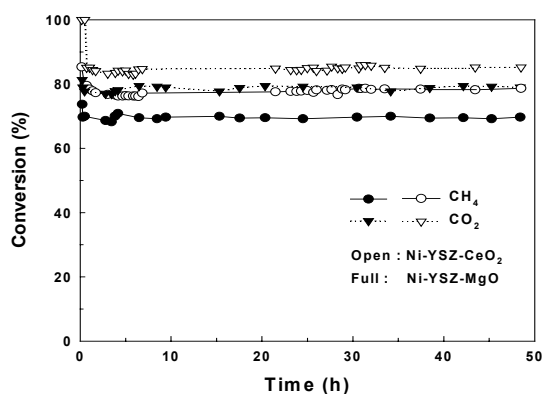


Fig. 2 The conversions of CO₂ and CH₄ with the time on stream over prepared catalyst at 800 °C.

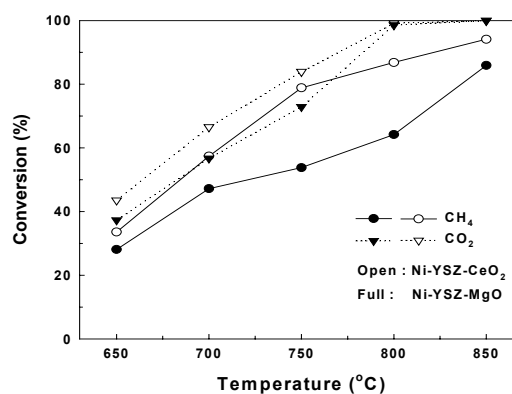


Fig. 3. The effect of reaction temperature on the conversion over the prepared catalyst.

Figure 3 shows the effect of reaction temperature on the conversions of CO₂ and CH₄ over the prepared catalysts. It was found that the Ni-YSZ-CeO₂ 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.

Table 1. The characteristics of prepared catalysts before and after the reaction

| Catalyst | Conditions | BET surface area (m ² /g) | Total pore volume (cc/g) | Active metal surface area (m ² /g) |
|-------------------------|-----------------|--------------------------------------|--------------------------|---|
| Ni-YSZ-CeO ₂ | before reaction | 10.2 | 0.004 | 0.098 |
| | after reaction | 15.7 | 0.007 | 0.076 |
| Ni-YSZ-MgO | before reaction | 8.9 | 0.003 | 0.081 |
| | after reaction | 13.4 | 0.005 | |

The characteristics of prepared catalysts before and after the catalytic reforming of CO₂ by CH₄ are summarized in Table 1. It was found that the BET surface area, total pore volume and active metal surface area of Ni-YSZ-CeO₂ catalyst were 10.2 m²/g, 4×10⁻³ cc/g and 0.098 m²/g, while those of the Ni-YSZ-MgO catalyst were 8.9 m²/g, 3×10⁻³ cc/g and 0.081 m²/g, respectively. Figure 4 and Figure 5 represent the X-ray diffraction (XRD) patterns of Ni-YSZ-CeO₂ and Ni-YSZ-MgO catalysts before and after the catalytic reforming of CO₂ by CH₄, respectively. It was found that NiC phase on the surface of the catalysts was produced after catalytic CO₂ reforming over Ni-YSZ-CeO₂ and Ni-YSZ-MgO catalysts, respectively. However, it was considered that the carbon deposited on the surface of the catalyst under the catalytic reforming was mainly desorbed to carbon dioxide by the reaction (C + O²⁻ → CO₂) of oxygen ion transferred from the cathode with the surface carbon over the electrochemical cell (Ni-YSZ-CeO₂ or Ni-YSZ-MgO | YSZ | (La,Sr)-MnO₃) in SOFC system.

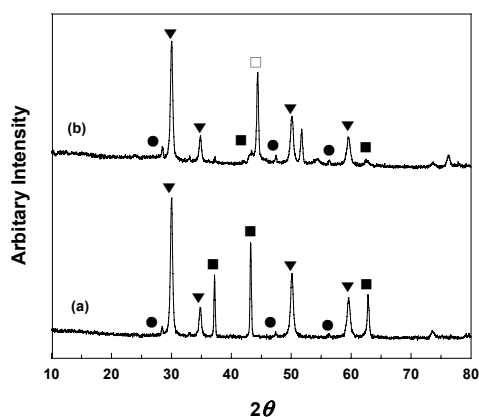


Fig. 4. XRD patterns of Ni-YSZ-CeO₂ catalyst before and after the catalytic reforming of CO₂ by CH₄. ■: NiO, □: NiC ▼: YSZ, ●: CeO₂ (a) before reaction (b) after reaction

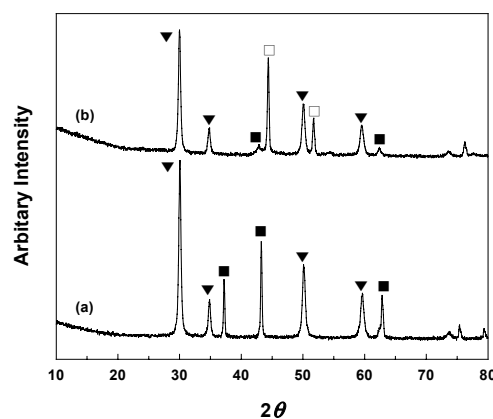


Fig. 5. XRD patterns of Ni-YSZ-MgO catalyst before and after the catalytic reforming of CO₂ by CH₄. ■: NiO, □: NiC ▼: YSZ (a) before reaction (b) after reaction

Temperature-programmed reduction (TPR) profiles of the catalysts were obtained by heating the samples from room temperature to 1100°C at a rate of 10°C/min, in a 5%H₂/Ar gas flow (50ml/min). TPR curves for Ni-YSZ-CeO₂ and NiO-YSZ-MgO catalyst are presented in Fig. 6. NiO showed a reduction peak at about 380°C and 580°C, respectively, CeO₂ exhibited a weak reduction peak at about 800°C, but YSZ did not show any reduction peak below 1100°C. It was found that a reduction peak at

380°C was registered in the spectra of Ni-YSZ based catalyst. It was suggested that the Ni-YSZ-CeO₂ catalyst could be applied as an anode catalyst to produce the syngas and electricity in the SOFC system.

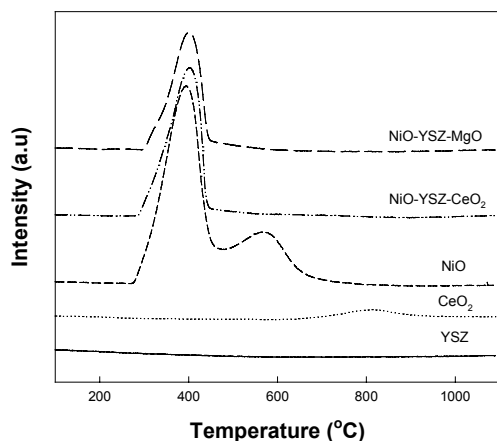


Fig. 6. TPR profiles of Ni-YSZ-CeO₂ and Ni-YSZ-MgO catalysts.

MgO catalyst at temperature range of 650~850°C and the maximum activity was observed at above 800°C. The H₂ and CO produced in the catalytic reforming can be applied as reactants in the SOFC system.

It was concluded that the Ni-YSZ-CeO₂ catalyst is a promising candidate for development as an anode material for an electrocatalytic reforming of CO₂ by CH₄ in the SOFC system.

Acknowledgement

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