

# Methane Steam Reforming over Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> loaded on Fe-Cr Alloy Honeycomb Monolith

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초록 : 에너지원으로서 수소를 생산하기 위하여 하니컴 구조를 갖는 모노리스에 10 wt% Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> 촉매를 담지한 후 메탄의 수증기 개질 실험을 수행하였다. 다른 CeO<sub>2</sub>/ZrO<sub>2</sub> 몰비를 갖는 촉매들 중에서, Ni/CeO<sub>2</sub>-ZrO<sub>2</sub>(CeO<sub>2</sub>/ZrO<sub>2</sub>=4/1) 촉매가 700-800°C에서 높은 메탄의 전환율을 보여 주었다. 10wt% Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> 촉매가 담지된 금속 모노리스 촉매체는 높은 열전도도와 비 표면적으로 인하여 좋은 촉매 특성을 보여줌을 확인할 수 있었다. 또한, 금속모노리스 촉매체는 반응물에서 과다의 수증기에 의한 수소 수율에서 크게 영향을 받지 않음을 알 수 있었다. GHSV=30,000h<sup>-1</sup>, 반응물 비(H<sub>2</sub>O/CH<sub>4</sub>=3.0) 반응온도 800°C에서 금속모노리스 촉매체는 98%이상의 메탄의 전환율을 보여주었다. 생성물 가스에서 CO<sub>2</sub>/CO의 비는 수증기/메탄의 반응물비가 증가할수록 수성가스화 반응에 의하여 증가됨을 알 수 있었다.

## 1. Introduction

A great number of the emerging interest in hydrogen technology has been focused on the automotive industry and fuel cells. Hydrogen fuel cell engines using proton exchange membrane technology are greener alternatives to batteries and generators. They are clean and quiet and produce no exhaust gases other than water vapor. Therefore, the paramount issue is how to provide the hydrogen gas. Up until now, several approaches to produce hydrogen such as steam reforming, partial oxidation, autothermal reforming, electrochemical, photochemical, biological and thermo-chemical methods have been carried out. Steam

reforming is one of the least expensive hydrogen production methods[1-3]. Much research work is concentrated on steam reforming of methane, hydrocarbon and ethanol etc[4-7]. Among the above fuels, methane, which makes up over 85 percent of natural gas, has the highest hydrogen-to-carbon ratio of any hydrocarbon. Thus, the majority of commercial hydrogen used today is produced by reforming natural gas.

Although hydrogen has the merit of clean energy, the usage of hydrogen is restricted due to the intrinsic properties of hydrogen and limitation in storage. The demand for on-site hydrogen supply equipments increases with the increasing needs for small size power suppliers such as fuel cells. Thus, the research on the development of a compact type of steam reforming device is required[8].

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Among the catalysts for steam and/or partial oxidation reforming of methane, the Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts showed outstanding activity, coking resistance and stability[6, 9-11]. It is well known that the remarkable catalytic performance of Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> is attributed to the combination of several advantages of high oxygen storage capacity of ceria in solid solution, strong interaction between Ni and CeO<sub>2</sub>-ZrO<sub>2</sub>, and high thermal stability of the CeO<sub>2</sub>-ZrO<sub>2</sub> solution[12-13].

In spite of the high activity and stability of Ni/CeO<sub>2</sub>-ZrO<sub>2</sub>, from the industrial point of view, this system is difficult to commercialize due to the high price of CeO<sub>2</sub>-ZrO<sub>2</sub>. Roh et al. tried to prepare CeO<sub>2</sub>-ZrO<sub>2</sub> layer onto a commercially available alumina supporter ( $\Theta$ -Al<sub>2</sub>O<sub>3</sub>) before impregnating Ni in order to decrease CeO<sub>2</sub>-ZrO<sub>2</sub> content[14]. They use the  $\Theta$ -Al<sub>2</sub>O<sub>3</sub> supporter instead of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> because  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> do not have the stability with time on stream during methane reforming reaction [15]. As a fast start-up reactor, a palladium wash coated metallic monolith catalyst which was equipped with an electrically-heated catalyst for partial oxidation of methane was reported[16]. A copper-based monolith was studied for steam reforming of methanol[17].

In this work, an alumina-coated honeycomb monolith structure of Fe-Cr alloy was employed as a supporter for the catalyst Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> in steam reforming of methane. We confirmed that Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> loaded on alumina-coated honeycomb monolith for the catalyst of steam reforming of methane has high catalytic activity because the honeycomb type catalyst has large specific surface area, high thermal conductivity and mechanical shock resistance and lower pressure drop. In addition, the Fe-Cr alloy honeycomb monolith can be easily fabricated into diverse modules for the industrial purpose. We also studied optimum composition of the catalyst Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> and operation conditions for the steam reforming of methane reaction.

## 2. Experimental

The CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst was prepared by co-precipitation of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and ZrOCl<sub>2</sub>·8H<sub>2</sub>O (Aldrich) in mole ratios Ce/Zr=1/3, 1/1, 3/1 and 4/1, respectively. Before metal solutions were mixed up together, 0.1 M of aqueous metal solutions were prepared and mixed up. Urea was added to the previous solution to become 0.4 M of urea solution. The resulted mixture was maintained at 100°C for 50h with stirring. It was cooled down to room temperature and filtered and washed with de-ionized water and ethanol to prevent agglutination of the particles. The resulted particles dried at 50°C for 2h within a rotating oven, and then heated 500°C for 4h in air. Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> was prepared by impregnation method with a Ni(NO<sub>3</sub>)<sub>2</sub> solution. The amount of the Ni(NO<sub>3</sub>)<sub>2</sub> solution added to the CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst was designed to have 10 wt% Ni in the CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst. The resulted mixture was dried at 50°C for 2h within a rotating evaporator. It was calcined at 800°C for 5h in air.

A honeycomb monolith was fabricated with the alloy (FE080210 Fecralloy®, GoodFellow Co.) as shown in Fig. 1. The size of the honeycomb is 2.0cm in diameter and height, respectively. The alloy was composed of Fe 72.8%, Cr 22%, Al 5%, Y 0.1%, Zr 0.1% and its thickness was 0.05 mm. The honeycomb structure was coated with alpha-alumina slurry and dried and heated in air.

The catalyst was also coated over the alumina coated honeycomb with a slurry form. The catalyst Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> was ground to powder having below 100  $\mu$ m in its size before loading. It was dried at 50°C for 4h and heated 900°C for 2h. Finally the honeycomb coated with catalyst was reduced in the flow of 5% H<sub>2</sub> in N<sub>2</sub> at 500°C for 2h. The BET specific areas and pore volumes of the Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> and CeO<sub>2</sub>-ZrO<sub>2</sub> having different compositions were measured by N<sub>2</sub>

adsorption at 77K (Autosorb-1MP, Quantachrome). The XRD patterns of the Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> were recorded with an X-ray diffractometer (Bruker, Siemen Co.) using Ni-filtered CuK $\alpha$  radiation on a flat sample holder. Surface analysis of the catalyst Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> was performed with a SEM (GAWA2, Teracan).

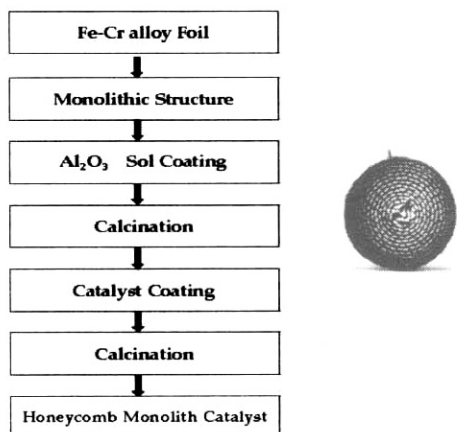


Fig. 1. Fabrication of Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst loaded on the alumina-coated honeycomb monolith.

Catalytic activity measurements for steam reforming of methane were conducted in two fixed bed stainless tube reactors mounted vertically inside a furnace. The one of reactors was 1/2 inch tube for the characterization of the powder Ni/CeO<sub>2</sub>-ZrO<sub>2</sub>, and the other reactor was 1 inch for the characterization of catalyst Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> loaded on the alumina-coated honeycomb. For the catalytic tests about 0.3 cm<sup>3</sup> of the powder form of Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> was loaded and one piece of the honeycomb catalyst was placed inside the reactors, respectively. The reactor temperature was monitored by a thermocouple placed at the outside of the reactor and measured by thermocouples inserted directly into both top and bottom layers of catalyst bed. Prior to each catalytic measurement, the catalyst was reduced in 5% H<sub>2</sub>/N<sub>2</sub> at 500°C for 2h. The mixed reactant

stream of methane and steam was supplied from the top of the reactor as shown in Fig. 2.

Water was injected using a micro-syringe and evaporated at 300°C. Reactant line was heated over 120°C. The product gases were analyzed by a gas chromatograph (ACDE6000, Younglin) using a column of Carboxen 1000.

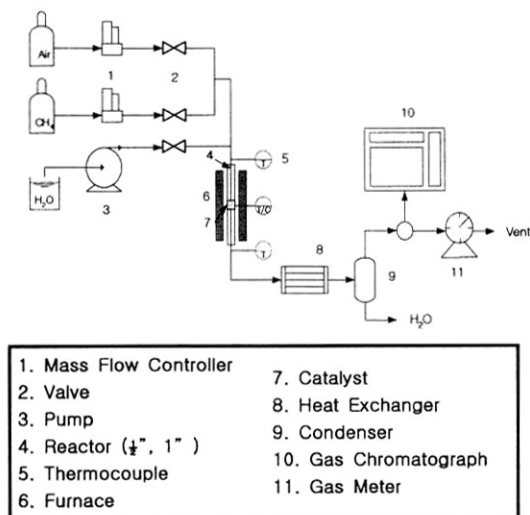


Fig. 2. Schematic diagram of the experimental set-up.

### 3. Results and Discussion

Pore volumes, surface areas and particle sizes of the CeO<sub>2</sub>-ZrO<sub>2</sub> samples (in mole ratios of Ce/Zr=1/1, 4/1) and the Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> samples (in mole ratios of Ce/Zr=1/1, 4/1) were investigated respectively, as shown in Table 1. The sample CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1) has larger pore volume (0.054 cm<sup>3</sup>/g) and surface area (76 m<sup>2</sup>/g) than the other. When 10 wt% of Ni was loaded on the support CeO<sub>2</sub>-ZrO<sub>2</sub>, the resulted particle sizes of Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> were increased, but surface areas and pore volumes were decreased. Particularly, the surface area of the CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1)

Table 1. Physical Properties of the Catalysts

Catalysts	Pore volume (cc/g)	BET (m <sup>2</sup> /g)	Particle size ( $\mu$ m)
CeO <sub>2</sub> -ZrO <sub>2</sub> (Ce/Zr=1/1)	0.035	50	42
Ni/CeO <sub>2</sub> -ZrO <sub>2</sub> (Ce/Zr=1/1)	0.016	22	51
CeO <sub>2</sub> -ZrO <sub>2</sub> (Ce/Zr=4/1)	0.054	76	37
Ni/CeO <sub>2</sub> -ZrO <sub>2</sub> (Ce/Zr=4/1)	0.015	20	48

was dramatically diminished by the loading of Ni content.

The XRD diffraction patterns of the three samples, CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr =1/1, 3/1 and 4/1), were given in Fig. 3. Lower intensity in XRD peaks was observed at the sample CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=1/1). In contrast to this, increased intensities in XRD peaks were observed from the samples CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=3/1) and CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1). The increased peaks were identified as those of cubic phase CeO<sub>2</sub>.

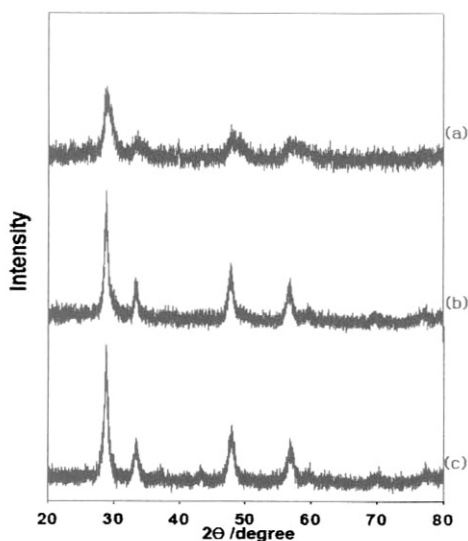


Fig. 3. XRD patterns of catalysts:  
 (a) CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=1/1)  
 (b) CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=3/1)  
 (c) CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1).

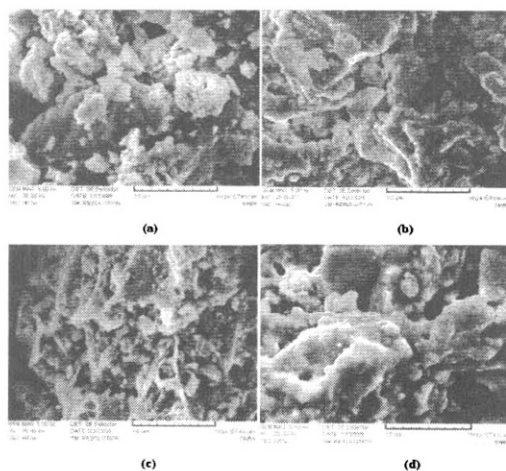


Fig. 4. SEM images of 10 wt% Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts.  
 (a) Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=1/1)  
 (b) Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=3/1)  
 (c) Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1)  
 (d) Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=1/1) loaded on an alumina-coated honeycomb monolith.

The SEM images of particles Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> are shown in Fig. 4. The particle shapes were changed from granular type to crosslink shape with increasing Ce content Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=1/1 → 4/1). The shapes of the catalyst Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=1/1) ((a) in Fig. 4) were similar with those of the catalyst Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> loaded on the honeycomb ((d) in Fig. 4). Heterogeneity in Ni element on the surface of catalysts was confirmed by EDS analysis. The content of Ni was varied from 9 wt% to 15 wt%

depending on the points measured. Also the surface area of the sample CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1), 76 m<sup>2</sup>/g, was diminished to 20 m<sup>2</sup>/g by the Ni loading (10 wt%). This means that most of the micro-pores were filled up with Ni particles, and Ni particles were mainly located on the outer surface of the catalysts. The catalysts Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> were characterized by the reaction of steam reforming of methane in the range of 500~800 °C as illustrated in Fig. 5.

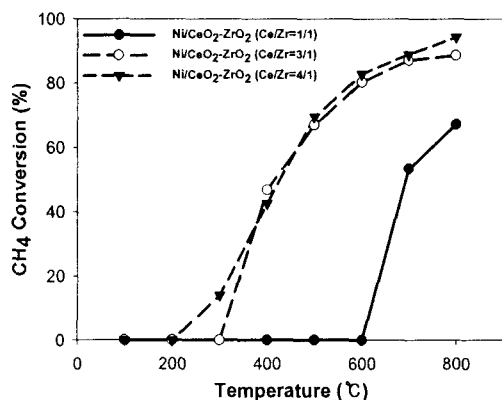


Fig. 5. Effect of temperature on steam reforming (SRM) over Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=1/1, 3/1 and 4/1) catalysts (reaction condition: GHSV=30,000h<sup>-1</sup>, Ni loading=10 wt%, H<sub>2</sub>O/CH<sub>4</sub>=3).

The catalyst Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1) shows the highest catalytic activities. It showed 94% conversion at 800°C. However, the catalysts Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=1/1) showed very poor catalytic activities. The product distributions of the steam reforming of methane over the Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> at 800°C were illustrated in Fig. 6. It is confirmed that both conversion and yield for H<sub>2</sub> were increased by increasing Ce content.

The catalytic activities of catalyst Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> loaded on the alumina coated honeycomb monolith were also tested by steam reforming of methane reaction. Compared to the powder form of

Ni/CeO<sub>2</sub>-ZrO<sub>2</sub>, the honeycomb types of catalyst show higher catalytic activities and yield for H<sub>2</sub> as illustrated in Fig. 7.

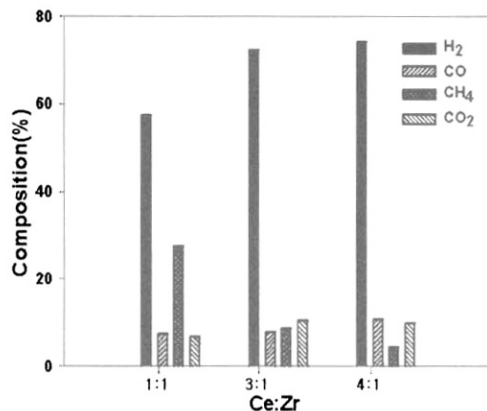


Fig. 6. Product distributions obtained from the catalysts (10 wt% Ni/CeO<sub>2</sub>-ZrO<sub>2</sub>) having various Ce/Zr ratios (reaction condition: GHSV=30,000h<sup>-1</sup>, H<sub>2</sub>O/CH<sub>4</sub>=3, T=800°C).

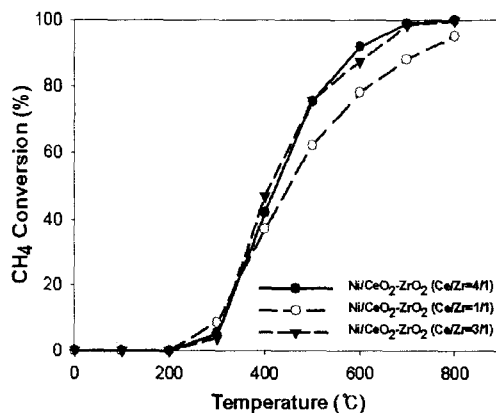


Fig. 7. Effect of temperature on steam reforming (SRM) over the Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=1/1, 3/1 and 4/1) catalysts loaded on the alumina-coated honeycomb monoliths (reaction condition: GHSV=20,000h<sup>-1</sup>, Ni loading=10 wt%, H<sub>2</sub>O/CH<sub>4</sub>=3).

Especially, the honeycomb coated with the Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=1/1) showed the largest increase in methane conversion from 64% at 500°C to 92% at 800°C, and the honeycomb catalysts having Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1, 3/1) showed over 99% conversion from 700°C. The feed rate GHSV=20,000h<sup>-1</sup> is considered very high because the honeycomb structure occupy large space compared to the packed catalyst bed (the amount of catalyst loaded on the honeycomb was about 10 wt% of the honeycomb). It is conformed that both conversion and yield for H<sub>2</sub> were increased by increasing Ce content, and honeycombs coated with Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> have good catalytic performance due to higher thermal conductivity and large specific contact area of the monolith. The product distributions of the steam reforming of methane over the catalyst Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1) loaded on alumina-coated honeycomb at 800°C were illustrated in Fig. 8. The CO selectivity, CO/(CO+CO<sub>2</sub>), increased with increasing reaction temperature.

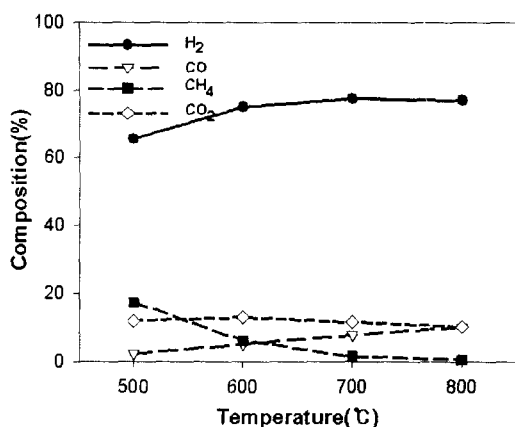


Fig. 8. Effect of temperature on the product distribution of steam reforming (SRM) over the Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1) catalysts loaded on the alumina-coated honeycomb monolith (reaction condition: GHSV=20,000h<sup>-1</sup>, Ni loading=10 wt%, H<sub>2</sub>O/CH<sub>4</sub>=3).

There are reports that catalytic activity of the Ni based catalysts decreased by excess steam in feeds[7]. In order to get the optimum inlet steam/methane ratio on the steam reforming reaction, influence of inlet H<sub>2</sub>O/CH<sub>4</sub> mole ratio on conversion was investigated at the reaction temperature of 800°C and GHSV 20,000h<sup>-1</sup>. Conversion of methane increases until the feed mole ratio (H<sub>2</sub>O/CH<sub>4</sub>) reaches 3.0, and then decreases there after as shown in Fig. 9. This trend was clearly observed from the conversion data resulted from the honeycomb catalysts coated with Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=3/1). This result was supported by the work of Laosiripojana and Assbumrungrat who reported that the steam reforming rate increased with increasing inlet H<sub>2</sub>O/CH<sub>4</sub> ratio until this ratio reached approximately 1.0-2.0 over Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=3, 4.8 wt% Ni) at the reaction temperature of 800°C[7]. They interpreted this phenomena as it was related to the decrease in oxidized state of the catalyst caused by the promotion of the water-gas shift reaction in the forward direction. However, conversions over the honeycombs coated with Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1) maintained highly although the inlet H<sub>2</sub>O/CH<sub>4</sub> ratio was over 3.0. It is deduced that the honeycomb catalyst coated with Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1) has a resistance to high hydrogen appearance caused by excess steam in feed. The ratio of CO<sub>2</sub>/CO in the products increases with the increased ratio of H<sub>2</sub>O/CH<sub>4</sub> due to the water-gas shift reaction.

Fig. 10 depicts the effect of space velocity on the catalytic activity of the honeycomb coated with Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1, 3/1) at 800°C. The weight of catalyst loaded on the honeycomb catalyst, 0.8 g, was about 10 wt% of the honeycomb catalyst. Methane conversion was reached to 98.8% when the space velocity was below 30,000h<sup>-1</sup>. Conversion and the ratio of CO/(CO<sub>2</sub>+CO) in

the products were slowly decreased with increasing space velocity. It is interpreted that CO produced reacts with excess steam and converts to CO<sub>2</sub> as shown in Table 2.

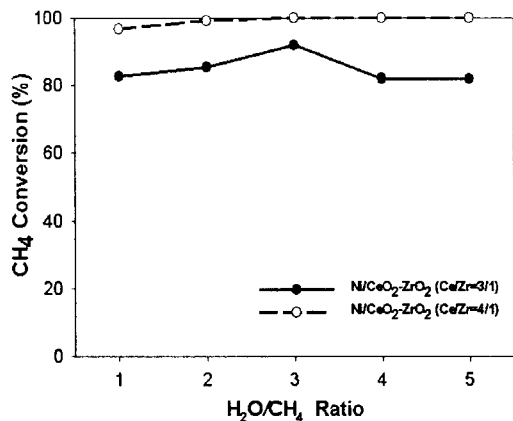


Fig. 9. Influence of inlet feed ratio (H<sub>2</sub>O/CH<sub>4</sub> in mol) on conversions acquired from the catalysts loaded on honeycomb monoliths (reaction condition: GHSV=20,000h<sup>-1</sup>, T=800°C).

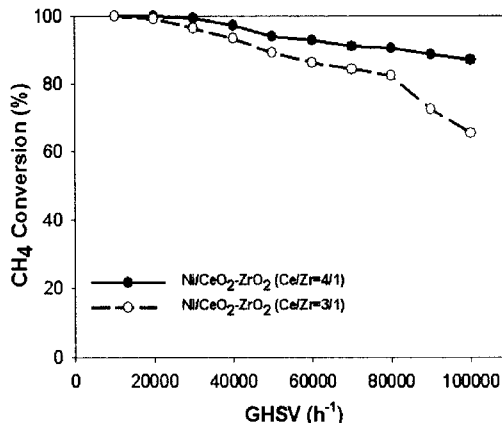


Fig. 10. Effect of the gas hourly space velocity (GHSV) on conversion (reaction condition: Ni loading=10 wt%, H<sub>2</sub>O/CH<sub>4</sub>=3, T=800°C).

#### 4. Conclusions

We showed that Fe-Cr alloy honeycomb monolith can be easily fabricated into a module for an industrial purpose. It was confirmed that both conversion and yield for H<sub>2</sub> were increased by increasing Ce content

Table 2. The Compositions of the Products on Various GHSV (H<sub>2</sub>O/CH<sub>4</sub>=3, T=800°C)

GHSV (h <sup>-1</sup> )	H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>
			(%)	
10,000	77.6	12.2	0.7	9.5
20,000	78.2	10.9	0.8	10.1
30,000	77.7	11.5	1.2	9.6
40,000	77.2	9.1	2.7	11.0
50,000	76.1	7.2	4.9	11.8
60,000	75.3	7.5	5.8	11.4
70,000	74.7	5.9	7.1	12.3
80,000	72.9	6.2	9.3	11.6
90,000	73.1	5.9	9.6	11.4
100,000	73.5	5.5	10.2	10.8

in 10 wt% Ni/CeO<sub>2</sub>-ZrO<sub>2</sub>. The catalyst Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> loaded on alumina-coated honeycomb monolith showed high catalytic activity in the reaction of steam reforming of methane reaction. The honeycomb coated with 10 wt% Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1) showed the best conversion (>99%) under space velocity 20,000h<sup>-1</sup> at 800°C. Conversion over the honeycombs coated with Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1) was maintained highly until the feed ratio (H<sub>2</sub>O/CH<sub>4</sub>) was over 3.0. It is deduced that the honeycomb catalyst coated with Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Ce/Zr=4/1) has a resistance to high hydrogen appearance caused by excess steam in feed. The ratio of CO<sub>2</sub>/CO in the products increases with the increased ratio of H<sub>2</sub>O/CH<sub>4</sub> due to the water-gas shift reaction. Conversion and the ratio of CO/(CO<sub>2</sub>+CO) in the products were slowly decreased with increasing space velocity. It is interpreted that CO produced reacts with excess steam and converts to CO<sub>2</sub>.

### Acknowledgments

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### References

1. M. M.V.M. Souza and M. Schmal, Autothermal Reforming of Methane over Pt/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Catalysts, *Appl. Catal. A*, **281**, 19 (2005).
2. S. Ahmed and M. Krumpelt, Hydrogen from Hydrocarbon Fuels for Fuel Cells, *J. hydrogen Energy*, **26**, 291 (2001).
3. K. Nagaoka, A. Jentys and J. A. Lercher, Methane Autothermal Reforming with and without Ethane over Mono- and Bimetal Catalysts Prepared from Hydrotalcite Precursors, *J. Catal.*, **229**, 185 (2005).
4. Y. H. Wang and J. C. Zang, Hydrogen Production on Ni-Pd-Ce/γ-Al<sub>2</sub>O<sub>3</sub> Catalyst by Partial Oxidation and Steam Reforming of Hydrocarbons for Potential Application in Fuel Cells, *Fuel*, **84**, 1926 (2005).
5. D. Srinivas, C. V. V. Satyanarayana, H. S. Potdar and P. Ratnasamy, Structural Studies on NiO-CeO<sub>2</sub>-ZrO<sub>2</sub> Catalysts for Steam Reforming of Ethanol, *Appl. Catal. A*, **246**, 323 (2003).
6. N. Laosiripojana and S. Assabumrungrat, Methane Steam Reforming over Ni/Ce-ZrO<sub>2</sub> Catalyst : Influences of Ce-ZrO<sub>2</sub> Support on Reactivity, Resistance toward Carbon Formation, and Intrinsic Reaction Kinetics, *Appl. Catal. A*, **290**, 200 (2005).
7. N. Laosiripojana, W. Sangtongkitcharoen and S. Assabumrungrat, Catalytic Steam Reforming of Ethane and Propane over CeO<sub>2</sub>-doped Ni/Al<sub>2</sub>O<sub>3</sub> at SOFC Temperature: Improvement of Resistance toward Carbon Formation by the Redox Property of Doping CeO<sub>2</sub>, *Fuel*, **85**, 323 (2006).
8. M. Krumpelt, R. Kumar and K. M. Myles, Fundamentals of Fuel Cell System in Integration, *J. Power Sources*, **49**, 37 (1994).
9. S. Xu and X. Wang, Highly Active and Coking Resistant Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> Catalyst for Partial Oxidation of Methane, *Fuel*, **84**, 563 (2005).
10. W. Wang, S. M. Stagg-Williams, F. B. Noronha, L. V. Mattos and F. B. Passos, Partial Oxidation and Combined Reforming of Methane on Ce-promoted Catalysts, *Catal. Today*, **98**, 553 (2004).
11. Z. Cheng, Q. Wu, J. Li and Q. Zhu, Effects of Promoters and Preparation Procedures on Reforming of Methane with Carbon Dioxide over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, *Catal. Today*, **30**, 147 (1996).
12. A. Muto, T. Bhaskar, Y. Kaneshiro, Y. Sakata, Y. Kusano and K. Murakami, Preparation and Characterization of



- Nanocrystalline CeO<sub>2</sub> - ZrO<sub>2</sub> Catalysts by Dry Method: Effect of Oxidizing Conditions, *Appl. Catal. A*, **275**, 173 (2004).
13. K. Kusakabe, K. Sotowa, T. Eda and Y. Iwamoto, Methane Steam Reforming over Ce - ZrO<sub>2</sub>-supported Noble Metal Catalysts at Low Temperature, *Fuel Proc. Technol.*, **86**, 319 (2004).
  14. H. S. Roh, K. W. Jun and S. E. Park, Methane-Reforming Reactions over Ni/Ce-ZrO<sub>2</sub>/θ-Al<sub>2</sub>O<sub>3</sub> Catalysts, *Appl. Catal. A*, **251**, 275 (2003).
  15. W. S. Dong, H. S. Roh, K. W. Jun, J. S. Chang, S. E. Park and Y. I. Joe, Highly Active and Stable Ni/Ce - ZrO<sub>2</sub> Catalyst for H<sub>2</sub> Production from Methane, *J. Mol. Catal. A*, **181**, 137 (2002).
  16. H. Jung, W. L. Yoon, H. Lee, J. S. Park, J. S. Shin, H. La and J. D. Lee, Fast Start-up Reactor for Partial Oxidation of Methane with Electrically-Heated Metallic Monolith Catalyst, *J. Power Sources*, **124**, 76 (2003).
  17. B. L. and L. J. Pettersson, Steam Reforming of Methanol over Copper-Based Monoliths: The Effects of Zirconia Doping, *J. Power Sources*, **106**, 264 (2002).