

## Ni catalyst wash-coated on metal monolith with enhanced heat-transfer capability for steam reforming

Jae-Hong Ryu<sup>a</sup>, Kwan-Young Lee<sup>a,\*</sup>, Howon La<sup>b</sup>, Hak-Joo Kim<sup>b</sup>, Jung-Il Yang<sup>b</sup>, Heon Jung<sup>b,\*\*</sup>

<sup>a</sup> Department of Chemical and Biological Engineering, Korea University, 5-1 Anam-dong, Sungbuk-ku, Seoul 136-701, South Korea

<sup>b</sup> Synthetic Fuel Research Center, Korea Institute of Energy Research, 71-2 Jang-dong, Yusong-ku, Daejeon 305-343, South Korea

Received 20 March 2007; accepted 20 May 2007

Available online 23 June 2007

### Abstract

A commercial Ni-based catalyst is wash-coated on a monolith made of 50  $\mu\text{m}$ -thick ferralloy plates. Compared with the same volume of coarsely powdered Ni catalysts, the monolith wash-coated Ni catalysts give higher methane conversion in the steam reforming reaction, especially at gas hourly space velocities (GHSV) higher than 28,000  $\text{h}^{-1}$ , and with no pressure drop. A higher conversion of the monolith catalyst is obtained, even though it contains a lower amount of active catalyst (3 g versus 17 g for a powdered catalyst), which indicates that the heat-transfer capability of the wash-coated Ni catalyst is significantly enhanced by the use of a metal monolith. The efficacy of the monolith catalyst is tested using a shell-and-tube type heat-exchanger reactor with 912  $\text{cm}^3$  of the monolith catalyst charged on to the tube side and hot combusted gas supplied to the shell side in a counter-current direction to the reactant flow. A methane conversion greater than 94% is obtained at a GHSV of 7300  $\text{h}^{-1}$  and an average temperature of 640  $^{\circ}\text{C}$ . Nickel catalysts should first be reduced to become active for steam reforming. Doping a small amount (0.12 wt.%) of noble metal (Ru or Pt) in the commercial Ni catalyst renders the wash-coated catalyst as active as a pre-reduced Ni catalyst. Thus, noble metal-doped Ni appears useful for steam reforming without any pre-reduction procedure.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Nickel catalyst; Metal monolith; Steam reforming; Noble metal doping; Heat-transfer enhancement; Hydrogen fuel cells

### 1. Introduction

With the recent advent of fuel cell technologies, intensification of hydrogen manufacturing processes is required, especially with respect to the steam-reforming reactor. The steam reforming of hydrocarbons over pelletized Ni catalysts is a well-known reaction but is subject to heat-transfer limitations. The difficulty of supplying a large amount of heat to the catalyst at high temperatures results in a large volume of steam reforming catalysts, with a superficial contact time of 0.4–1.5 s. This corresponds to a GHSV (gas hourly space velocity) of between 2500 and 8900  $\text{h}^{-1}$  [1,2]. A superficial contact time of less than 10 ms has been reported in the literature, including integrated methane steam reforming and combustion on the adjacent side of the reactor [3–5]. Heat-transfer enhancement also increases the ther-

mal efficiency of the endothermic reaction system due to higher utilization of heat sources [4].

Compact reactors, with a high throughput, should employ catalysts with a certain shape to attain a minimum pressure drop. Monolith catalysts provide channels for easy flow of reactants, with pressure drops that are one to two orders of magnitude less than those obtained with packed-beds. In addition, monoliths made of metal possess improved radial heat-transfer characteristics because their cellular structure has a high thermal conductivity, which provides a continuum for radial heat-transfer compared with the edge and point contacts of the pellet catalysts used in a packed-bed reactor [6]. In our previous work, the promoted Pd catalyst wash-coated on the metal monolith was found to be a good catalyst for the partial oxidation of methane at a high GHSV, due to the more uniform temperature resulting from its inherently high thermal conductivity [7]. In this work, Ni catalysts wash-coated on to a metal monoliths are prepared and used in heat-exchanger type reactors for the methane steam reforming reaction. The aim is to increase the heat-transfer capability of the Ni catalyst for the manufacture of compact steam reformers.

\* Corresponding author. Tel.: +82 2 3290 3299; fax: +82 2 926 6102.

\*\* Co-corresponding author. Tel.: +82 42 860 3663; fax: +82 42 860 3134.

E-mail addresses: [kylee@korea.ac.kr](mailto:kylee@korea.ac.kr) (K.-Y. Lee), [jungh@kier.re.kr](mailto:jungh@kier.re.kr) (H. Jung).

Nickel-based steam reforming catalysts should be reduced in the presence of hydrogen before the introduction of hydrocarbon reactants [1] to obtain a high activity at lower temperatures. After the shut down of a reactor, especially when the Ni catalyst has been steamed, the recommended procedure is to reduce the catalyst again to restore its full activity [1]. For reformers with frequent on–off cycles, a steam reforming catalyst without the need of reduction will make the system and operating procedure much simpler. In this study, the Ni catalyst is modified to allow it to become active at low temperatures, without a pre-reduction procedure.

## 2. Experimental

### 2.1. Preparation of metal monolith wash-coated Ni catalyst

A commercial Ni-based steam reforming catalyst (21 wt.% Ni on MgO and Al<sub>2</sub>O<sub>3</sub>) was washcoated on to a metal monolith. Cylindrical, pellet type, Ni catalysts were crushed into fine particles (less than 40 mesh). The Ni catalyst powders were slurry in 5 M HNO<sub>3</sub> solution, and then further ball-milled for 16 h.

The method of preparing the cylindrical metal monolith has been explained elsewhere [7]. The monolith was made with 50 μm-thick fecralloy plates (Goodfellow Co.), with a cell density of about 640 cpi and a size of 2.2 cm (diameter) × 2 cm (height). The monolith was pre-oxidized to enhance the adhesion between the ceramic-type Ni catalyst and the metal monolith. The calcined monoliths were dipped into the slurry containing the Ni catalysts and then dried at room temperature. This process was repeated several times until the desired amount of catalyst had been washcoated (0.2 g of wash-coated catalyst per 1 cm<sup>3</sup> of the monolith).

The coated catalyst was dried further in an oven at 120 °C for 1 h, and then calcined in a temperature-programmed manner, namely: heated from 20 to 121 °C for 1 h, from 121 to 232 °C for 1 h, from 232 to 565 °C for 2 h and from 565 to 900 °C for 2.5 h, with the upper temperature after each stage held for 30 min. After completion of the heating process, the catalyst was allowed to cool to room temperature within the furnace.

A small amount of noble metal was doped into the Ni catalyst to serve as a reduction-enhancing agent. Prior to the doping, the Ni-coated monolith was pre-calcined to 565 °C, and then dipped into a solution containing the desired amount of noble metal precursors. The noble metal incorporated catalyst was calcined to 900 °C using the same program mode outlined above. RuCl<sub>3</sub> (RuCl<sub>3</sub>·xH<sub>2</sub>O, Aldrich Chem. Co.), H<sub>2</sub>PtCl<sub>6</sub> (H<sub>2</sub>PtCl<sub>6</sub>·xH<sub>2</sub>O, Aldrich Chem. Co.) and H<sub>2</sub>Cl<sub>6</sub>Ir (H<sub>2</sub>Cl<sub>6</sub>Ir·xH<sub>2</sub>O, Aldrich Chem. Co.) were used as the noble metal precursors.

### 2.2. Characterization of the catalysts

The BET surface areas of the catalysts were measured using an ASAP 2010 (Micromeritics) instrument. The powder X-ray diffraction (XRD) patterns of the catalysts were obtained by means of using a Rigaku D/max 2000 ultima plus diffractometer (monochromatic nickel filter, Cu Kα radiation). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES, 138

Ultace, Jobin Yvon) analysis was performed to determine the composition of the catalyst.

### 2.3. Catalytic reaction

The methane steam reforming activity of the catalyst was tested in a tubular quartz reactor (inside diameter of 2.22 cm) that was operated at atmospheric pressure. Without noble metal doping, the Ni catalyst was reduced in a stream of H<sub>2</sub> at 600 °C for 1.5 h prior to the reaction. For doped Ni catalysts, the steam reforming reaction was initiated without the pre-reduction treatment.

Methane (CH<sub>4</sub>, 99.999%) and steam were used as the reactants, with the H<sub>2</sub>O:CH<sub>4</sub> ratio maintained at 3. During the reaction, two temperatures were measured: one before the catalyst bed and the other at the exit of the catalyst bed.

Heat-exchanger reactors constructed from stainless-steel were also used. The monolith catalysts were charged on to the tube side, with the hot exhaust gas passed through the shell side. Two different types of heat-exchanger reactors were employed, namely, a single-tube reactor and a six-tube reactor, both of which had 1 in. diameter pipes.

The compositions of the products were analyzed with a gas chromatograph (HP5890, TCD) equipped with a Porapak Q column (8.2 ft × 1/8 in.). The conversion of methane was calculated based on the flow rate and product gas composition.

## 3. Results and discussion

### 3.1. Powdered catalyst versus metal monolith wash-coated catalyst

Fig. 1 shows the XRD pattern of the Ni-based catalyst. The as-received catalyst was in the form of NiO supported on an MgAl<sub>2</sub>O<sub>4</sub> solid solution. The surface area of the fresh catalyst was 19.7 m<sup>2</sup> g<sup>-1</sup> (Table 1). After acid treatment (to allow better bonding on to the metal surface) and calcination at 900 °C, the surface area slightly decreased to 16.2 m<sup>2</sup> g<sup>-1</sup>.

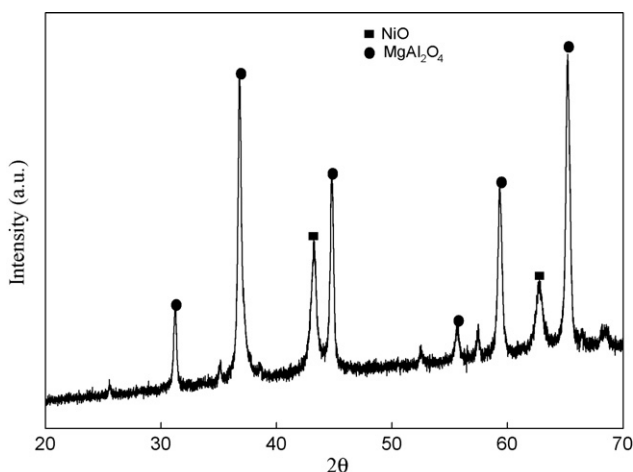


Fig. 1. The XRD pattern of commercial Ni-based steam reforming catalyst.

Table 1  
BET surface area of selected commercial Ni catalysts

Catalyst	Calcination temperature (°C)	Surface area (m <sup>2</sup> g <sup>-1</sup> )
Fresh	–	19.2
After acidic treatment	900	16.2
After acidic treatment and Ru doping	900	15.8

The temperature-programmed steam methane reforming reaction ( $\text{H}_2\text{O}:\text{CH}_4 = 3$ ) was carried out over two of the 2.2 cm (diameter)  $\times$  2 cm (height) metal monoliths wash-coated with the above Ni-based catalyst. The GHSV, which was calculated based on the reactant flow rate at room temperature and the volume of the monoliths, was 9443 h<sup>-1</sup>. The temperature-programmed steam methane reforming reaction was also run at the same GHSV over the same volume of coarsely powdered Ni catalyst (average diameter 3–4 mm), and the results are compared in Fig. 2. In the case of particles smaller than 1 mm in diameter, a severe pressure drop is experienced at GHSVs higher than 5000 h<sup>-1</sup>.

Temperatures were measured at two locations, i.e., one before the catalyst bed and the other at the exit of the catalyst. Since steam reforming is a severe endothermic reaction, the exit temperature is lower than the front-end temperature by as much as 20 °C at a GHSV of 9443 h<sup>-1</sup>. In Fig. 2, the exit temperatures were employed since the reaction is closer to equilibrium under the conditions near to the exit, with the conversion calculated from the composition of the exit products. The trends of the activity–temperature relationship are very similar, even when the front temperature is employed. The metal monolith wash-coated Ni catalyst gives a higher methane conversion, by as much as 20%, than the powdered catalyst. The weight of the catalyst charged in 15.2 cm<sup>2</sup> of the reactor was 17 g for the powdered catalyst, while the net weight of the Ni catalyst wash-coated in 15.2 cm<sup>3</sup> of the monolith was 3 g. The higher methane conversion obtained with the monolith catalyst, despite the less amount of active catalyst material, indicates that the heat-

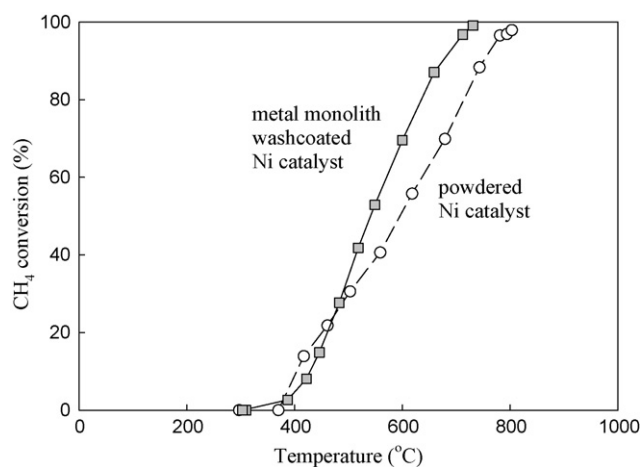


Fig. 2. Comparison of temperature-programmed steam methane reforming reactions; powdered Ni catalyst vs. metal monolith wash-coated Ni catalyst, catalyst volume: 15.2 cm<sup>3</sup>, GHSV = 9443 h<sup>-1</sup>.

transfer capability of the Ni catalyst is significantly enhanced by the use of the metal monolith. In the modelling study of Flytzani-Stephanopoulos et al. [6], the temperature at the centres of the metal monolith during the steam reforming reaction was calculated to be much higher than that of the pelleted catalysts with the same dimensions. The higher centres temperature of the metal monolith catalyst was due to the higher rate of heat-transfer from the outer reactor wall via conductive heat-transfer by the metal monolith. The supply of more heat to the catalyst on the metal monolith eases the heat-transfer limitation, which results in better utilization of the active steam reforming catalyst. On the other hand, the radial heat-transfer of the pelletized catalysts relies on the convective action of gaseous material, which is less efficient.

Catalyst particles wash-coated on to the monolith were ball-milled to very fine sizes to increase their adhesion to the metal surfaces. Thus, the effectiveness factor for the wash-coated catalyst particles is close to unity, which leads to better utilization of the catalyst. The net result is an increase in the catalytic activity.

To investigate further the efficacy of metal monolith catalysts for steam reforming, the GHSV was increased in the two catalytic set-ups outlined above. Attempts were made to maintain the catalyst exit temperatures close to 730 °C. The results of the study are shown in Fig. 3. At GHSVs less than 20,000 h<sup>-1</sup>, the methane conversions of both the catalytic systems are similar when the temperature is higher than 730 °C. With GHSVs higher than 28,000 h<sup>-1</sup>, however, the methane conversion of the metal monolith catalyst is about 10% higher than that of the powdered Ni catalysts, even at lower exit temperature. Because of the limited heating capacity of the electric furnace, the catalyst bed exit temperature could not be raised when the magnitude of the endothermic reaction became large due to the high GHSVs. A much larger difference in the methane conversion would be expected when the exit temperatures of the metal monolith catalyst bed are equal to those of the powdered catalyst bed. The results in Fig. 3 clearly demonstrate the superiority of the steam reforming catalyst wash-coated on to the metal monolith, due to increases in both the heat-transfer capability and the effectiveness factor.

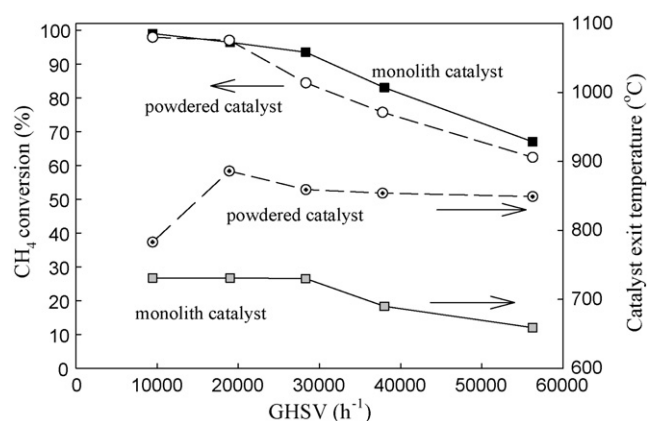


Fig. 3. Change in methane conversion of steam reforming reaction as function of GHSV (powdered Ni catalyst vs. metal monolith wash-coated Ni catalyst).

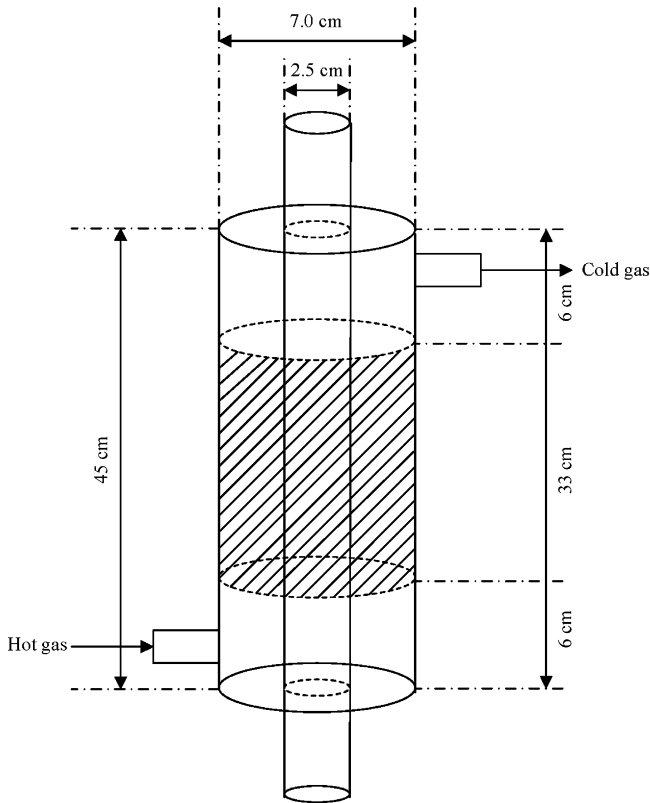


Fig. 4. Single-tube heat-exchanger reactor.

### 3.2. Single-tube heat-exchanger reactor

Five Ni catalyst wash-coated metal monoliths, 2.2 cm (diameter)  $\times$  2 cm (height) in size, were charged in the stainless-steel

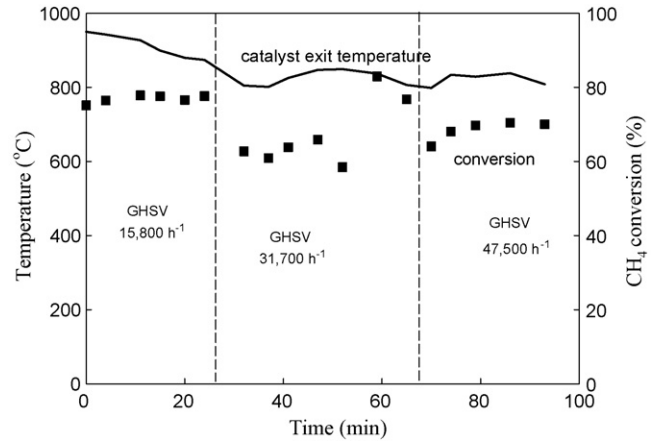


Fig. 6. Performance of single-tube heat-exchanger reformer at various GHSVs.

tube (1-in. OD) of a single-tube heat-exchanger reactor (Fig. 4). The hot exhaust gas from a catalytic combustor passed through the shell side in a counter-current direction to the reactant flow. Fig. 5 shows a schematic of the reformer system. Air for the catalytic combustion was initially heated by a heat-exchanger and then by an in-line heater prior to mixing with the methane. A Pd-based ceramic monolith was used as a combustion catalyst, with an electrically heated catalyst (EHC) used as an ignition device for the combustor. The reforming catalysts were pre-reduced using hydrogen. Once the average temperature of the catalyst bed had attained about  $850^{\circ}\text{C}$ , the steam methane reforming reaction was initiated. As shown in Fig. 6, the methane conversion is about 80% at a GHSV of  $15,800\text{ h}^{-1}$ . When the reactant flow is increased to a GHSV of  $47,500\text{ h}^{-1}$ , there is only a slight decrease in the methane conversion to 70%, and

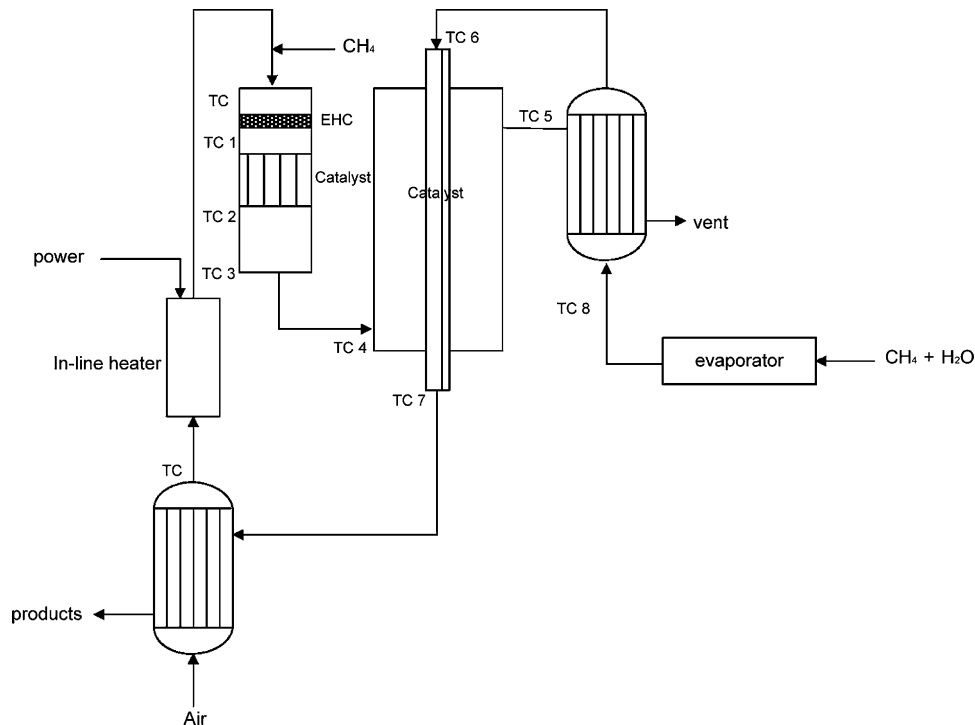


Fig. 5. Reforming system of single-tube heat-exchanger reactor and catalytic combustor.

with no detectable pressure drop. This observation suggests that compact steam reformers can be manufactured using Ni catalyst wash-coated metal monoliths and heat-exchanger type reactors.

### 3.3. Activity of Ni metal monolith catalyst doped with noble metal

As shown in Fig. 1, the as-received Ni-based steam reforming catalyst contained nickel in an oxide form (NiO). However, NiO is not active for steam reforming, especially at low temperatures [1]. Thus, most reforming catalysts are pre-reduced in the presence of hydrogen to gain a high activity. NiO catalysts can also be reduced by a mixture of natural gas and steam, but the reformer exit temperature has to be at least 750 °C, while the inlet temperature should be maintained as high as possible to expedite the reduction by natural gas [1].

The steam reforming reaction of methane was conducted over an unreduced NiO catalyst wash-coated on to the metal monolith. As shown in Fig. 7, no steam reforming reaction occurs at temperatures below 700 °C. As practiced in commercial reduction by natural gas, the unreduced NiO catalyst is reduced by methane and shows appreciable steam reforming activity at temperatures higher than 750 °C. By contrast, the NiO catalyst pre-reduced by hydrogen gives steam reforming activity at temperatures as low as 400 °C.

A pre-reduction procedure requires a reducing gas and several flow-controlling devices, which makes the reforming system complicated especially for small reformers. Small amounts of noble metal were doped into the NiO catalyst in order to obviate the pre-reduction treatment. The addition of Ru to a cobalt catalyst is known to facilitate the reduction of cobalt for the Fischer–Tropsch synthesis reaction [8,9]. Here, 0.12 wt.% of Pt, Ru or Ir was impregnated into the NiO-based catalysts, and the steam reforming reaction was run over those impregnated catalysts without any pre-reduction (Fig. 7). The Ru-doped catalyst starts to show steam reforming activity at temperatures as low as 450 °C, and then the activity increases with increasing reaction temperature; thereby, acting very similarly to the reduced

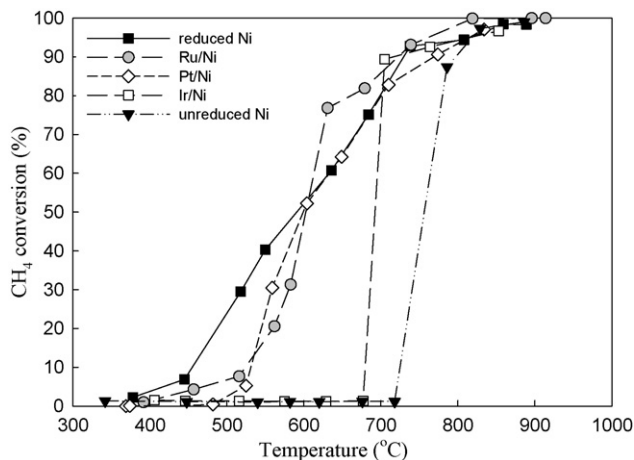


Fig. 7. Temperature-programmed steam reforming activity of various Ni catalysts (reduced vs. unreduced and noble metal-doped vs. no dopant) (GHSV = 9000 h<sup>-1</sup>, H<sub>2</sub>O:CH<sub>4</sub> = 3).

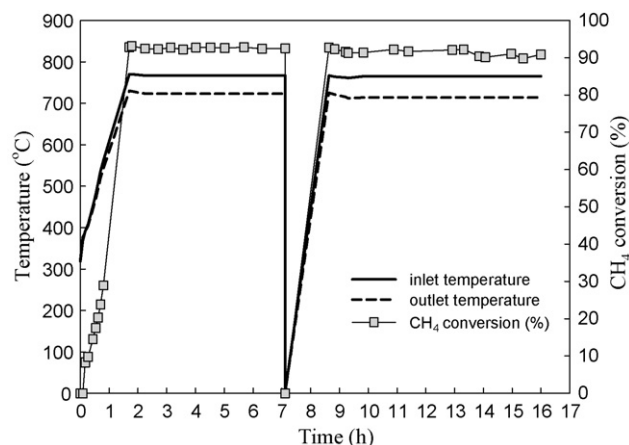


Fig. 8. Change in steam reforming activity of Ru/Ni catalyst wash-coated on to metal monolith during an on-off operation (GHSV = 9000 h<sup>-1</sup>, H<sub>2</sub>O:CH<sub>4</sub> = 3).

Ni catalyst. The addition of Pt also facilitates the reduction of NiO by methane, but at a higher temperature than the Ru-doped NiO catalyst. It is not as effective as Ru or Pt at increasing the reducibility of NiO catalysts.

When methane is adsorbed on to a metal surface at elevated temperatures, it decomposes to form carbidic surface carbon and hydrogen [10–13]. This decomposition takes place at lower temperatures over noble metals than over transition metals, such as Fe or Ni. With noble metals, such as Ru or Pt, methane decomposes at temperatures as low as 250 °C. The hydrogen generated by methane decomposition over either Ru or Pt might spill over to the nearby NiO, where it may be used as a reducing agent. The carbidic carbon on the noble metal surface can react with steam and convert to CO, thus regenerating the metal surface.

An on-off cyclic operation was performed over the Ru-doped Ni steam reforming catalyst wash-coated on to the metal monolith without any reduction treatment either prior to the reaction or in-between cycles. Again, the steam reforming reaction is initiated at about 400 °C over the catalyst with no pre-reduction (Fig. 8). After 6 h of stable reaction at 760 °C, the catalyst was cooled to room temperature in an environment containing steam, and maintained at room temperature overnight. The catalytic activity recovered to its previous level by just heating to the same reaction temperature of 760 °C. No reduction was performed prior to resumption of the reaction. Fig. 8 also demonstrates the durability of the Ru-doped Ni catalyst wash-coated on to the metal monolith during the on-off operation. The use of noble metal-doped Ni catalysts can make both the reforming system and operating procedure much simpler, especially for reformers with frequent on-off cycles.

### 3.4. Multi-tube heat-exchanger reactor

For the large-scale application of metal-monolith-based reforming catalysts, a shell-and-tube type heat-exchanger reactor was manufactured (Fig. 9). The monolith catalysts were charged in six stainless-steel tubes, each of 2.54 cm in diameter and 44 cm in length. Each tube contained twenty 2.2 cm (diameter) × 2 cm (height) Ru/Ni metal monolith catalysts, and the a

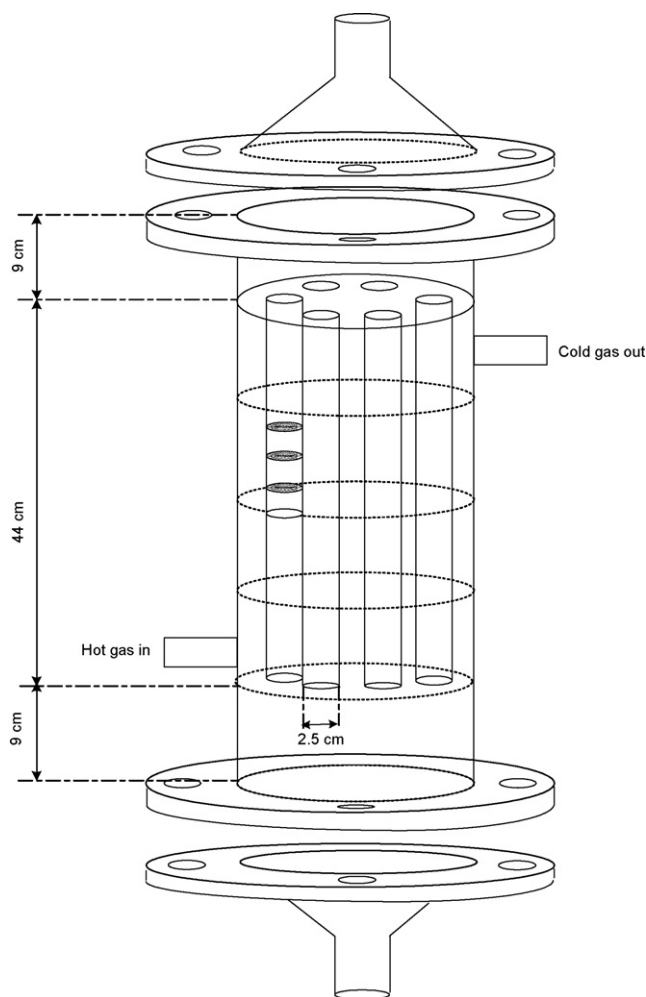


Fig. 9. Six-tube heat-exchanger reactor.

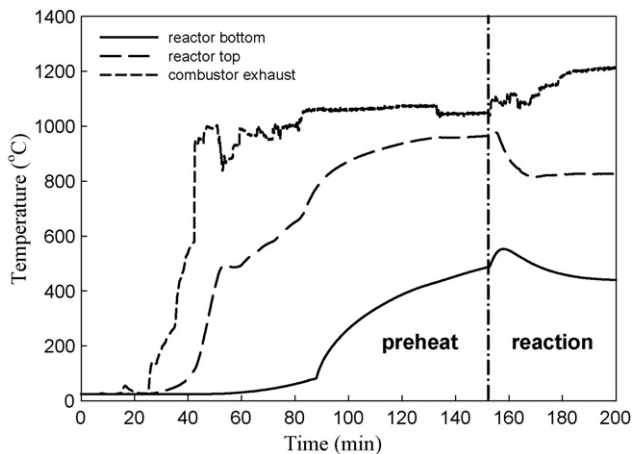


Fig. 11. Change in temperature during large-scale reforming.

total catalyst volume was 912 cc. The heat for the reaction was provided by hot gas from a catalytic combustor passing through the shell side of the reactor in the counter-current direction to the reactant flow. Steam and methane were premixed, and then preheated by a heat-exchanger prior to feeding into the reactor (Fig. 10).

Fig. 11 shows the temperature profile during the initial reformer start-up period. The reactor was flushed with flowing nitrogen during the heating period. Once the reactor exit gas temperature reaches 960 °C, the reactant mixture is introduced. The exit temperature then decreases to 830 °C due to the endothermic steam reforming reaction. The reactor inlet temperature is 450 °C. The average temperature of the whole catalyst bed is calculated to be about 640 °C. Methane ( $27.71 \text{ min}^{-1}$ ) and steam ( $83.11 \text{ min}^{-1}$ ) are used as the reactants and the GHSV is  $7300 \text{ h}^{-1}$ . The methane conversion is 94%. The composition of the product gas is listed in Table 2. The reformer shown in Fig. 9 has a fairly compact reactor volume of 131 and the volume of

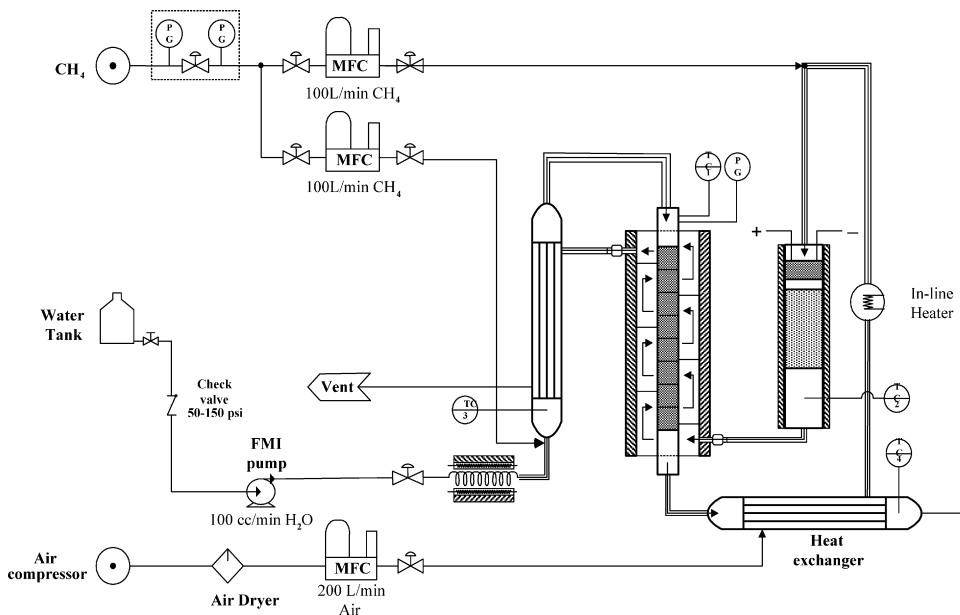


Fig. 10. Reforming system employing six-tube heat-exchanger reformer.

Table 2  
Composition of products from six-tube reformer

	Product			
	H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>
Concentration (%)	78.0	10.5	1.45	10.4

the catalytic combustor is about 10 l. The reforming system generates 5.46 and 0.78 m<sup>3</sup> h<sup>-1</sup> of hydrogen and CO, respectively, which is equivalent to a reformer fuelling a 6.2-kW PEM fuel cell.

#### 4. Conclusion

A structured steam reforming catalyst, in the form of a Ni catalyst wash-coated on a metal monolith, shows a higher steam reforming activity than the same volume of powdered catalyst due to increases in both the heat-transfer capability and the effectiveness factor. The difference in the activities is larger at higher GHSV, where the monolith catalyst has the added advantage of a lower pressure drop. Doping of a small amount (0.12 wt.%) of noble metal (Pt and Ru) on to the commercial Ni catalyst increases the activity to that of a pre-reduced Ni catalyst for steam reforming. The Ru-doped Ni catalyst wash-coated on to the metal monolith is tested on a larger-scale in a shell-and-tube heat-exchanger reactor. Syngas is produced at a rate of 6.2 m<sup>3</sup> h<sup>-1</sup> with 912 cm<sup>3</sup> of the monolith catalyst charged in the tube side, with hot combusted gas supplying the heat for the reac-

tion on the shell side. A methane conversion of 94% is obtained at a GHSV of 7300 h<sup>-1</sup> and average temperature of 640 °C.

#### Acknowledgements

This study was supported by SK Corporation, Korean Ministry of Commerce, Industry and Energy and the National RD&D Organization for Hydrogen & Fuel Cell.

#### References

- [1] J.R. Rostrup-Nielsen, *J. Catal.* 31 (1973) 173.
- [2] S.S. Bharadwaj, L.D. Schmidt, *Fuel Process. Technol.* 42 (1995) 109–127.
- [3] A.Y. Tonkovich, B. Yang, S.T. Perry, S.P. Fitzgerald, Y. Wang, *Catal. Today* 120 (2007) 21–29.
- [4] A.Y. Tonkovich, S. Perry, Y. Wang, D. Qiu, T. LaPlante, W.A. Rogers, *Chem. Eng. Sci.* 59 (2004) 4819–4824.
- [5] C. Cao, Y. Wang, R.T. Rozmiarek, *Catal. Today* 110 (2005) 92–97.
- [6] M. Flytzani-Stephanopoulos, G.E. Voecks, T. Charng, *Chem. Eng. Sci.* 41 (1986) 1203.
- [7] H. Jung, W.L. Yoon, H.T. Lee, J.S. Park, J.S. Shin, H.W. La, J.D. Lee, *J. Power Sources* 124 (2003) 76.
- [8] E. Iglesia, S.L. Soled, R.A. Fiato, G.H. Via, *J. Catal.* 143 (1993) 345.
- [9] N. Tsubaki, S. Sun, K. Fujimoto, *J. Catal.* 199 (2001) 236.
- [10] M. Bellgued, P. Pareja, A. Amarglio, H. Amarglio, *Nature* 352 (1991) 789.
- [11] M. Bellgued, A. Amarglio, P. Pareja, H. Amarglio, *J. Catal.* 159 (1996) 441.
- [12] M. Bellgued, A. Amarglio, P. Pareja, H. Amarglio, *J. Catal.* 159 (1996) 449.
- [13] T. Koerts, R.A. Santen, *J. Chem. Soc. Chem. Commun.* (1991) 1282.