Catalysis Today 156 (2010) 49–57

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

A diesel fuel processor for stable operation of solid oxide fuel cells system: I. Introduction to post-reforming for the diesel fuel processor

Sangho Yoon, Joongmyeon Bae *

Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology (KAIST), 335 Gwahangno, Yuseong-gu, Daejeon 305-701, Republic of Korea

ARTICLE INFO

Article history:
Available online 6 February 2010

Keywords:
Hydrogen
Diesel
Autothermal reforming (ATR)
Post-reforming

ABSTRACT

In this paper, a new concept of diesel fuel processing is introduced for the stable operation of solid oxide fuel cells (SOFCs). High temperature operation of SOFCs can lead to the capability of internal reforming with fuel flexibility. SOFCs can directly use CH_4 and CO as fuels given sufficient steam feeds due to catalytic reaction on the SOFC anode. However, heavier hydrocarbons than CH_4, such as ethylene, ethane, propane, etc., induce carbon deposition on the Ni-based anode of SOFCs. In the case of an ethylene steam reforming reaction on the Ni-based catalyst, the rate of carbon deposition is faster than it is when hydrocarbons, including aromatics, are used. Hence, the removal of light hydrocarbons (over C_1-hydrocarbons), especially ethylene, with the reformate gases of heavy hydrocarbons (diesel, gasoline, kerosene, and JP-8) is important for stable operation of SOFCs. A new methodology, called the "post-reformer", is introduced for removing the light hydrocarbons (over C_1-hydrocarbons) with the reformate gas stream. The CGO-Ru (3.0 wt.%) catalyst was selected as the post-reforming catalyst because it shows high selectivity for removing light hydrocarbons (over C_1-hydrocarbons) and achieving the high reforming efficiency. The diesel reformer and post-reformer are continuously operated for about 200 h in an integrated mode. The reforming performance did not degrade, and light hydrocarbons (over C_1-hydrocarbons) in the diesel reformate were completely removed.

1. Introduction

Due to global warming issues and the depletion of fossil fuels, fuel cells are receiving increased attention as electrochemical conversion devices [1,2]. Fuel cells are classified according to their operating temperature. Typical examples of high temperature fuel cells and low temperature fuel cells are the solid oxide fuel cell (SOFC) and the polymer electrolyte membrane fuel cell (PEMFC), respectively. Each type of fuel cell has its particular advantages. SOFCs have some merits due to the high operating temperatures, such as high system efficiency and fuel flexibility. Fuel flexibility, which is one in strong points of SOFCs, is essential in the application of the fuel cell system. The operation of the SOFCs does not rely on pure hydrogen as a fuel, but may also use carbon monoxide and light hydrocarbons [3,4]. The anode material of the SOFCs can internally reform CO and CH_4 into hydrogen due to its capability to steam reform (SR) [Eq. (1)] and catalyze the water-gas shift (WGS) [Eq. (2)] reactions [5]. It is possible that a wide range of fuels, including natural gas (NG), liquefied petroleum gas (LPG), and liquid hydrocarbon fuels, can be used by the SOFCs system.

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$

Although the diesel reformate contains higher concentrations of light hydrocarbons (CH_4, C_2H_4, C_3H_8, etc.) than other hydrocarbons (NG and LPG) reformate, diesel has attracted considerable attention as a hydrogen source for the SOFC system. The attraction of diesel fuels is due to the fuel flexibility of SOFCs and the merits of diesel reforming [4]. For hydrogen production, diesel has some advantages, such as high hydrogen density and existing refueling infrastructure. Diesel reforming also poses several problems. These include the high content of light hydrocarbons (over C_1-hydrocarbons) in the reformate, the occurrence of carbon deposition, the poisoning of reforming catalysts by sulfur, and difficulties in delivering diesel fuel to the reforming reactors. Among the several reforming methods available (i.e., steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR)), ATR is the most appropriate for guaranteeing long-term performance because it minimizes carbon deposition in diesel reforming [6–9]. However, the ATR reformate still contains the light hydrocarbons

---

* Corresponding author. Tel.: +82 42 350 3045; fax: +82 42 350 8207.
E-mail address: jmbae@kaist.ac.kr (J. Bae).

0920-5861/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.cattod.2010.01.006

(over C_1-hydrocarbons) in the ATR product gas, which induces carbon deposition on the Ni-based anode of the SOFCs.

Theoretically, it is possible for the SOFC anode to use the hydrocarbons. In our previous research, we found that SOFCs could directly use CH_4 as a fuel given sufficient steam feeds. Methane can be internally reformed very well by an electrochemical reaction on the anode of the SOFC at $H_2O/CH_4 \geq 1.5$ [10]. However, catastrophic performance degradation of the SOFC is induced by the supply of the C_2H_4 or normal-C_4H_{10} as a fuel at $H_2O/CH_4 \geq 1.5$ [11]. Rostrup-Nielsen et al. identified C_2H_4 as a severe carbon precursor to rapid carbon deposition on the Ni-based catalyst during the SR reaction [12]. The catalytic SR reaction of hydrocarbons on the Ni-based catalyst is similar to the reaction of the reformate that includes the light hydrocarbons on the Ni-based anode of SOFCs. Ethylene in the reformate causes rapid carbon deposition on the anode of the SOFCs [13]. Carbon deposition from light hydrocarbons (especially C_2H_4) in the reformate is an important issue that must be suppressed to guarantee stable operation of the SOFC system. The ethylene concentration is higher than the concentration of other hydrocarbons in the diesel reformate, and the ethylene concentration in the reformate clearly increases with decreasing reforming performance in diesel reforming [6,14,15]. It is necessary to remove all hydrocarbons except the CH_4 in the diesel reformate for suppression of carbon deposition on the anode of the SOFC.

In this paper, a new concept for diesel fuel processing, called "post-reforming", is introduced for removing the light hydrocarbons (over C_1-hydrocarbons) with the reformate gas stream. The objective, the decomposition of light hydrocarbons (over C_1-hydrocarbons), of both post-reforming and pre-reforming is the same [16,17]. However, the temperature of the post-reforming reaction is slightly higher than that for the pre-reforming reaction. Generally, the range of pre-reforming temperatures is from 300 °C to 500 °C. In a self-sustaining diesel ATR, the temperature of reformate is about 450–600 °C, so the temperature of the post-reforming reaction is in this range.

The commercial catalyst (Ni-based catalyst) of pre-reforming was used for post-reforming tests, but the Ni-based catalyst exhibited some problems, such as the need to use hydrogen for the reduction process and the ease of carbon deposition over the Ni catalyst. Hence, several novel metal catalysts were tested to select an effective catalyst for post-reforming. Finally, a commercial diesel ATR was operated with a post-reforming process.

2. Experimental

2.1. Microreactor test

A schematic diagram of the microreactor used in this study for the diesel ATR with the post-reforming reaction is shown in Fig. 1. The reactants for the diesel ATR are fuel, water, and air. The reformate of the diesel ATR is supplied directly to the post-reformer. In the case of the post-reforming catalyst test, the diesel ATR reactions were carried out at an O_2/C ratio = 0.5 and a $H_2O/C = 2$, with a synthetic fuel feed. Our previous research has shown that synthetic diesel I, a mixture of n-$C_{12}H_{26}$ and $C_{11}H_{10}$ (n-$C_{12}H_{26}$: 70 vol%; $C_{11}H_{10}$: 30 vol%), is in a good agreement of performance with commercial diesel [6]. After each catalyst test, both ATR and post-reforming microreactors were changed to new microreactors. In the case of the long-term performance test, the reaction was carried out at an O_2/C ratio = 0.8 and a $H_2O/C = 3$, with a commercial diesel (GS-caltex, Korea) feed for comparison to previous research results [6]. The fuel and de-ionized water (>15 MΩ) were supplied by an HPLC (high performance liquid chromatography) pump (MOLEH Co. Ltd.). The air and N_2 were regulated using a mass flow controller (MKS Co. Ltd.). The ATR and post-reforming reactors were made from a 12.7 mm STS (stainless steel) tube and placed inside an electrical furnace to maintain the reforming temperature. A gas hourly space velocity (GHSV) of 12,500 h^{-1} was selected, and the temperature of the electrical furnace was set at 800 °C for the ATR reaction. The post-reforming test was performed at a variety of reaction temperatures on various catalysts. The reaction conditions of all experiments are indicated in each figure caption.

2.2. Catalysts

The ATR reforming catalyst of Pt on Gd-doped CeO_2 (CGO-Pt) used in this study is a noble metal-based catalyst [18]. For the post-reforming test, a conventional pre-reforming catalyst (C11-PR from Süd-Chemie) was first obtained in the form of pellets, and then several catalysts, such as CGO-Pt (0.5 wt.%), CGO-Ru (0.5 or

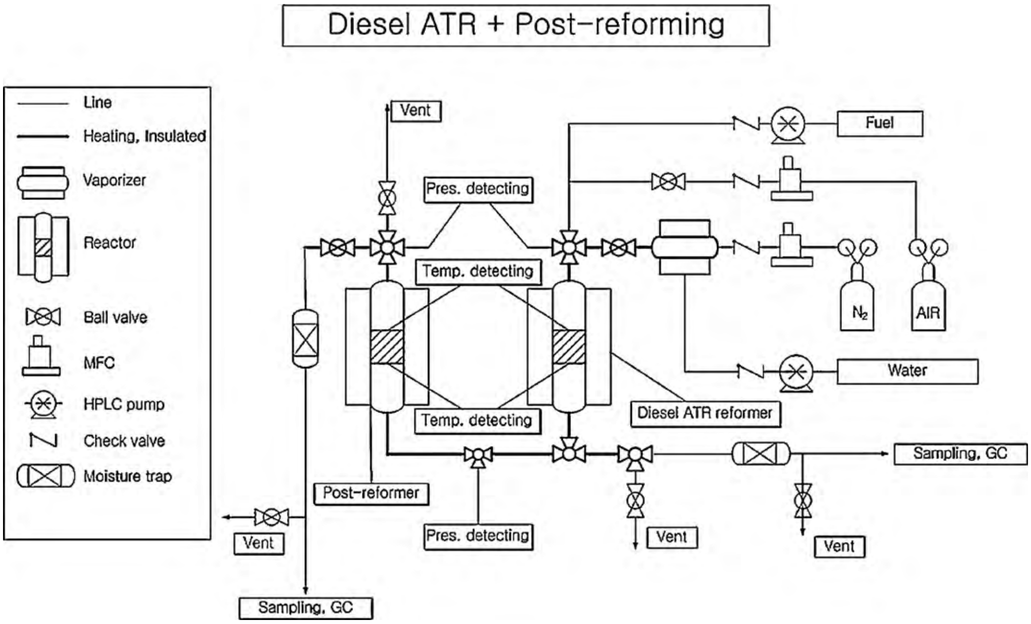

Fig. 1. Schematic diagram of the microreactor system.

Table 1
Catalysts used for reformation.

Catalysts	BET surface area (m^2/g)	Active metal surface area (m^2/g)	Fabrication method	Supplier
CGO-Pt (0.5 wt.%)	35.11	0.96	Combustion spray method	Praxair
CGO-Ru (0.5 wt.%)	35.90	1.22	Combustion spray method	Praxair
CGO-Ni (1.0 wt.%)	22.98	0.79	Combustion spray method	Praxair
CGO-Ru (3.0 wt.%)	26.50	2.22	Incipient wetness method	Home made
C11-PR	Unknown	Unknown	Unknown	Süd-Chemie

3.0 wt.%), and CGO-Ni (1.0 wt.%), were used. The full list of catalysts that were studied is displayed in Table 1. Chemisorption measurements were taken according to the procedure of previous research [19]. Unfortunately, characteristics of C11-PR commercial catalyst were not measured due to confidence. The catalysts of CGO-Pt (0.5 wt.%), CGO-Ru (0.5 wt.%), and CGO-Ni (1.0 wt.%) were synthesized via combustion spray pyrolysis by Praxair. The CGO-Ru (3.0 wt.%) catalyst was prepared using the incipient wetness of the CGO with aqueous solutions of the corresponding metal nitrates. The properties of the C11-PR catalyst are described in Table 2 [20]. The Ni-based catalysts, C11-PR and CGO-Ni (1.0 wt.%), were treated by a hydrogen reduction process before using them in experiments. The catalysts bed was maintained at approximately 600 °C for 4 h. Several research results mentioned that if Ni-based catalyst was not reduced appreciably with H_2 it was inactive in reforming reaction. It is, therefore, important to have pre-reduction treatment using H_2 for high activation and deactivation of resistant catalyst [21,22].

In the case of the post-reforming catalyst test, 2 ml of the ATR catalyst and 3.5 ml of the post-reforming catalysts were charged in each reactor. In the case of long-term test of diesel reforming with post-reforming, 1 ml of the ATR catalyst and 1.75 ml of the post-reforming catalyst were packed in the reactors.

2.3. Analytical

The water present in the product, ATR reformate and post-reforming reformate gases, was removed using a moisture trap, and the gases were then analyzed by gas chromatography (Agilent 6890N). The gas chromatograph consists of a TCD (thermal conductivity detector) and an FID (flame ionization detector). The concentrations of H_2, CO, CO_2, O_2, and N_2 were determined with the TCD. The FID analyzed the relative amounts of hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, i-C_4H_{10}, and n-C_4H_{10}).

Reforming efficiency, a measure of the reforming performance, is defined in Eq. (3). This value was used to analyze the possibility of using CH_4 as a fuel in SOFCs. For comparison of post-reforming catalysts, conversion of light hydrocarbons (over C_1-hydrocarbons) in post-reforming was determined and is defined in Eq. (4). Reformate compositions were represented in number of moles produced by 1 mol of supplied fuel.

$$\text{Reforming efficiency}\,(\%) = \frac{\text{LHV of}\,H_2 + CO + CH_4}{\text{LHV of fuels}} \tag{3}$$

$$\text{Conversion of light hydrocarbons (over } C_1\text{-hydrocarbons) } (\%) = \frac{\begin{array}{c}\text{total moles of light hydrocarbons (over } C_1\text{-hydrocarbons)}\\ \text{in the ATR reformate} - \text{total moles of light hydrocarbons}\\ \text{(over } C_1\text{-hydrocarbons) in the post-reforming reformate}\end{array}}{\begin{array}{c}\text{total moles of light hydrocarbons}\\ \text{(over } C_1\text{-hydrocarbons) in the ATR reformate}\end{array}} \tag{4}$$

Table 2
Properties of the C11-PR catalyst [20].

Components	Nickel	MgO	Al_2O_3	Promoter
Concentration (%)	45	10	10	Confidential

For comparison, the carbon tolerance was determined for the C11-PR and CGO-Ru (0.5 wt.%) catalysts. This was done by loading the post-reforming reactor with catalyst and running the reactor for 60 h at the same conditions as in the integrated mode. After the reaction, the qualitative analysis of carbon deposited on all of the reactors (ATR reactor and post-reforming reactor) was done using the TPO (temperature-programmed oxidation) method. The temperature was increased at the rate of 5 °C/min from 18 °C to 950 °C while air flowed through the chamber (500 ml/min at STP). The CO and CO_2 contents were quantified by FT-IR (Fourier transform-infrared spectrometry, FTPA2000, CIC Photonics, Inc.).

3. Results and discussion

Several research results have shown that complete conversion of the light hydrocarbons (over C_1-hydrocarbons) is difficult during the diesel reforming reaction [14,15]. As the operation time of the diesel reformer increases, the concentration of light hydrocarbons increases rapidly. If this product gas is directly supplied to the SOFC anode, stable operation of the SOFC is not guaranteed because the carbon deposition on the anode is induced by the light

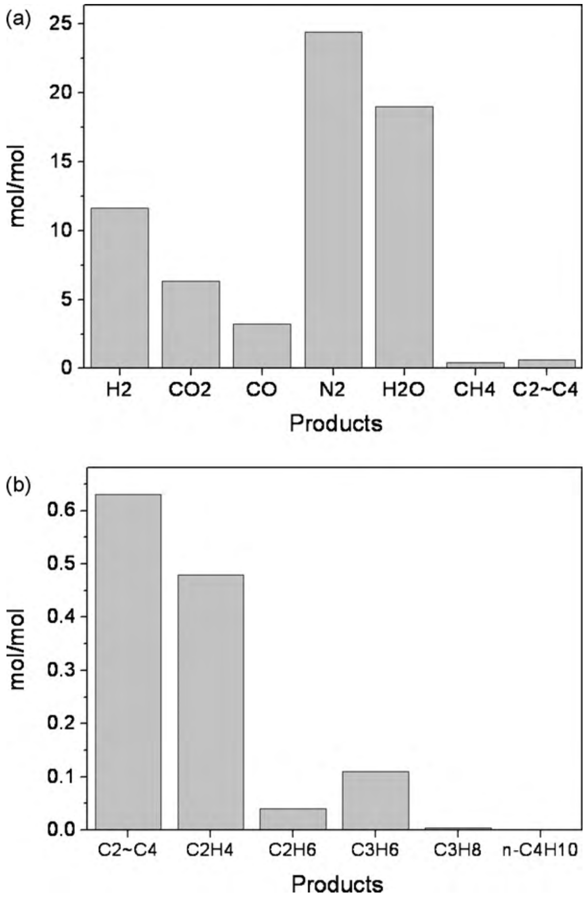

Fig. 2. Product distribution of the diesel ATR. ATR catalyst (CGO-Pt (0.5 wt.%)) volume = 2 ml; GHSV = 12,500 h^{-1}; H_2O/C = 2; O_2/C = 0.5; ATR temperature = 800 °C.

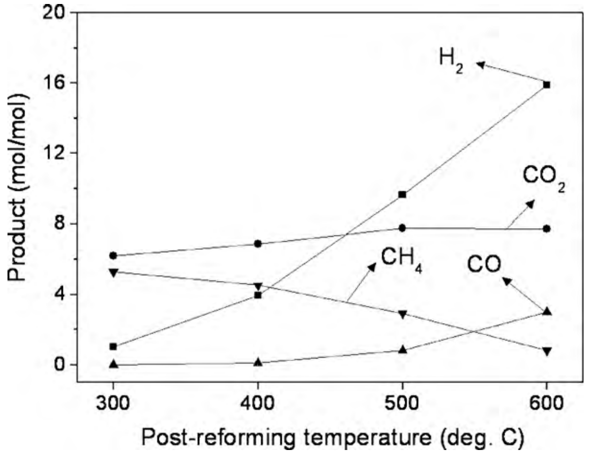

Fig. 3. Product distribution of post-reforming at several post-reforming temperatures. ATR catalyst (CGO-Pt (0.5 wt.%)) volume = 2 ml; GHSV = 12,500 h^{-1}; $H_2O/C = 2$; $O_2/C = 0.5$; ATR temperature = 800 °C; post-reforming catalyst (C11-PR) volume = 3.5 ml.

hydrocarbons (over C_1-hydrocarbons) in the diesel reformate. Although hydrogen is used and a low concentration of ethylene is present in the fuel, even with the addition of sufficient steam to SOFC anode, the performance of the SOFC is severely degraded by carbon deposition [23]. Hence, post-reforming is necessary to complete the conversion of light hydrocarbons (over C_1-hydrocarbons) in the diesel ATR reformate. The product distribution of the diesel ATR reformate is shown in Fig. 2, and this reformate is directly supplied to the post-reforming reactors. Oxygen of ATR reactants was entirely converted during ATR reaction. Water distribution was calculated by hydrogen balance and oxygen balance between inlet reactants and reformate, because water in the reformate was removed by a moisture trap.

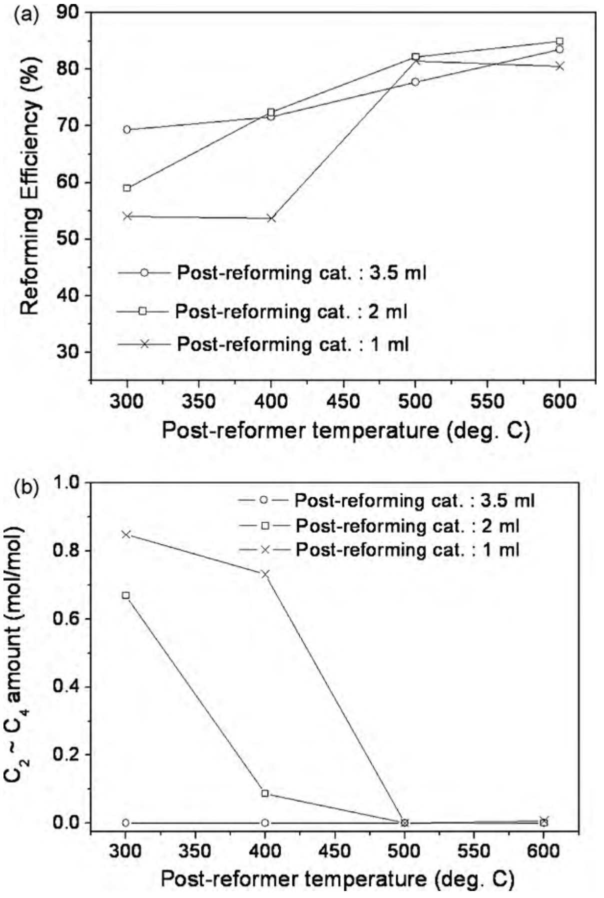

Fig. 4. (a) Reforming efficiency and (b) light hydrocarbon amounts in product gas vs. post-reforming catalyst (C11-PR) volume. ATR catalyst (CGO-Pt (0.5 wt.%)) volume = 2 ml; GHSV = 12,500 h^{-1}; $H_2O/C = 2$; $O_2/C = 0.5$; ATR temperature = 800 °C; post-reforming catalyst (C11-PR) volume = 1–3.5 ml.

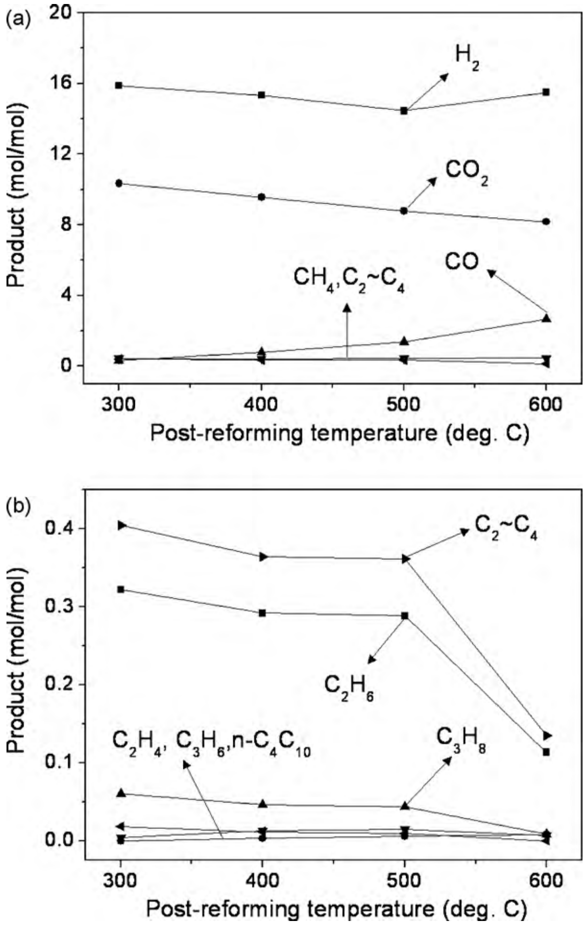

Fig. 5. Product distribution of post-reforming at several post-reforming temperatures. ATR catalyst (CGO-Pt (0.5 wt.%)) volume = 2 ml; GHSV = 12,500 h^{-1}; $H_2O/C = 2$; $O_2/C = 0.5$; ATR temperature = 800 °C; post-reforming catalyst (CGO-Pt (0.5 wt.%)) volume = 3.5 ml.

First, the residual light hydrocarbons (over C_1-hydrocarbons) were removed using the commercial pre-reforming catalyst C11-PR. Fig. 3 shows the result of the product distribution of post-reforming under various reforming temperatures with the C11-PR as the commercial catalyst. Light hydrocarbons (over C_1-hydrocarbons) were completely converted into other products through the reaction between the light hydrocarbons (over C_1-hydrocarbons) and steam in the reformate. At a post-reforming temperature of 600 °C, yields of hydrogen and carbon dioxide increased more than yields of the ATR reformate due to the WGS reaction between carbon monoxide and steam. Yields of hydrogen and carbon monoxide decreased, whereas yields of methane and carbon dioxide increased at reforming temperatures up to and including 500 °C. In this temperature range, the reformate from the ATR reacts not only by the WGS reaction but also by the methanation reaction [Eq. (5)] of CO and H_2. However, the methanation reaction is dominant at reforming temperatures up to and including 500 °C.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{5}$$

We investigated the effects of the GHSV and the temperature of the post-reforming reaction. Amounts of 1–3.5 ml of C11-PR

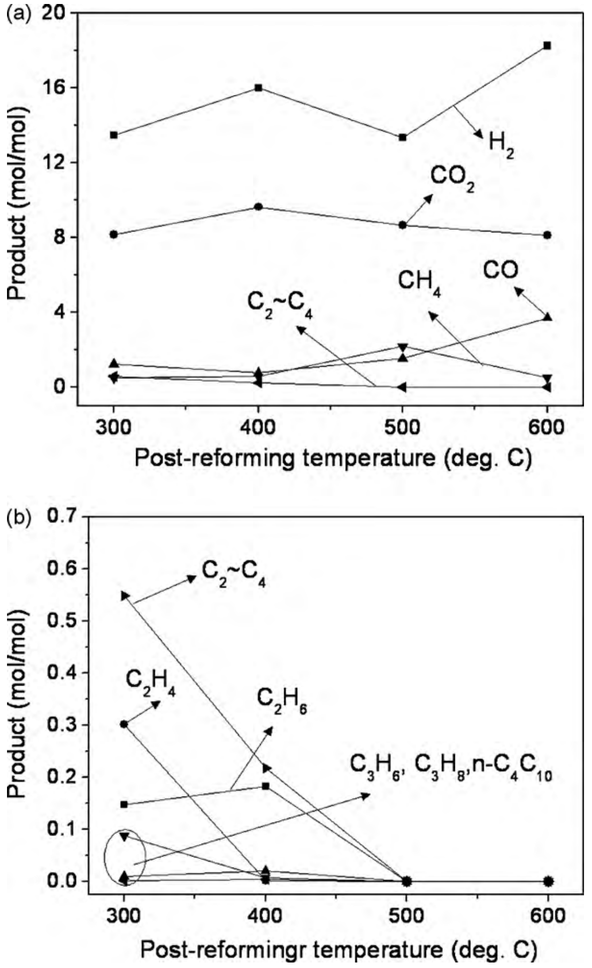

Fig. 6. Product distribution of post-reforming at several post-reforming temperatures. ATR catalyst (CGO-Pt (0.5 wt.%)) volume = 2 ml; GHSV = 12,500 h^{-1}; $H_2O/C = 2$; $O_2/C = 0.5$; ATR temperature = 800 °C; post-reforming catalyst (CGO-Ru (0.5 wt.%)) volume = 3.5 ml.

catalysts were loaded into the post-reformer to investigate the effects of the GHSV. The relationship between the post-reforming catalyst and the ATR reformate volume was calculated according to the GHSV, and the range of the GHSV values in the post-reforming reactor was about 10,000–30,000 h^{-1}. The reforming efficiency and the amounts of residual light hydrocarbons (over C_1-hydrocarbons) from the post-reforming reformate are shown in Fig. 4 as functions of the post-reforming temperature. The reforming efficiency decreases as the post-reforming temperature decreases from 600 °C to 300 °C, and the amounts of residual light hydrocarbons (over C_1-hydrocarbons) increase with decreasing temperature. When the GHSV in post-reforming was about 10,000 h^{-1}, the reaction temperature did not matter for removing the residual light hydrocarbons (over C_1-hydrocarbons). However, when the GHSV was 20,000 h^{-1} or more in post-reforming, residual light hydrocarbons (over C_1-hydrocarbons) in the ATR reformate did not completely convert at reforming temperatures up to and including 400 °C. Because the H_2 and CO in the ATR reformate were also converted by the methanation reaction, the reforming efficiency clearly decreased at reforming temperatures up to and including 400 °C. In the case where the C11-PR catalyst was used for post-reforming, the GHSV of post-reforming remained under 20,000 h^{-1}, and the post-reforming temperature remained over 500 °C, achieving both complete conversion of light hydrocarbons (over C_1-hydrocarbons) and high reforming efficiency.

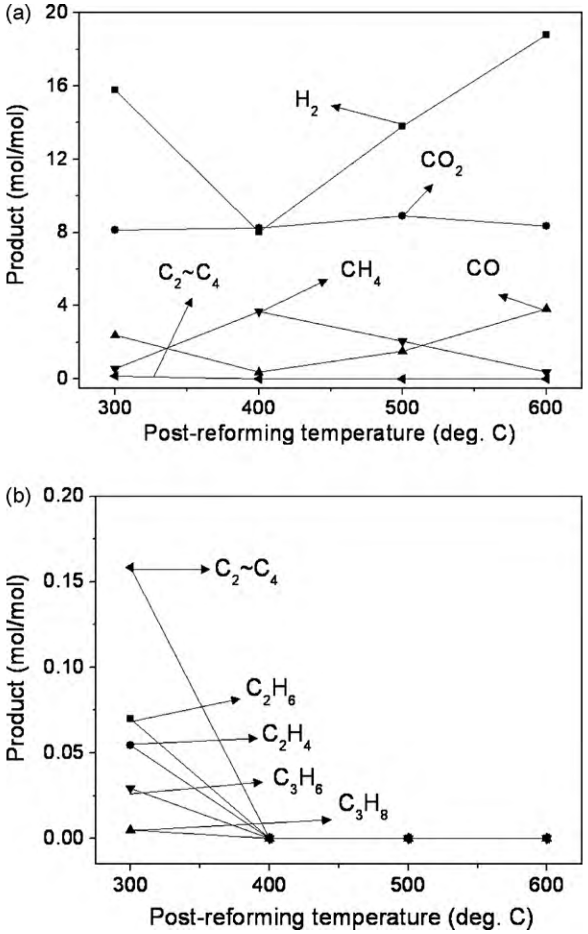

Fig. 7. Product distribution of post-reforming at several post-reforming temperatures. ATR catalyst (CGO-Pt (0.5 wt.%)) volume = 2 ml; GHSV = 12,500 h^{-1}; $H_2O/C = 2$; $O_2/C = 0.5$; ATR temperature = 800 °C; post-reforming catalyst (CGO-Ru (3.0 wt.%)) volume = 3.5 ml.

Although light hydrocarbons (over C_1-hydrocarbons) in the ATR reformate were effectively converted by the C11-PR post-reforming catalyst, this catalyst is difficult to use for large-scale reformer applications. This difficulty arises because a hydrogen reduction process is required for Ni-based catalysts. If a diesel reformer is used for SOFC systems of mobile, auxiliary power units (APU) and small-sized electric generation systems (the 1–5 kW-class), it is difficult to supply the systems with hydrogen due to the large system size and the lack of hydrogen infrastructure. In addition, the Ni-based catalyst has a lower tolerance to carbon deposition. Because of these reasons, some noble metal-based catalysts, such as Pt and Ru, were investigated for post-reforming.

Fig. 5 shows the amounts of the products of post-reforming under various reforming temperatures with the CGO-Pt (0.5 wt.%) catalyst. The CGO-Pt catalyst was not effective in converting light hydrocarbons (over C_1-hydrocarbons) under the whole range of post-reforming temperatures. At 600 °C, the light hydrocarbons (over C_1-hydrocarbons) were only slightly converted. Like in the previous experiment with the C11-PR catalyst, the water-gas shift reaction occurred. At reforming temperatures up to and including 500 °C, on the other hand, the methanation reaction was not dominant for the CGO-Pt catalyst, but, instead, the WGS and hydrogenation reactions dominated. The dominance of the WGS reaction was validated by increasing the amounts of H_2 and CO_2, and decreasing the amount of CO. Dominance of hydrogenation reaction was validated by increasing the amounts of C_2H_6 and C_3H_8 and decreasing the

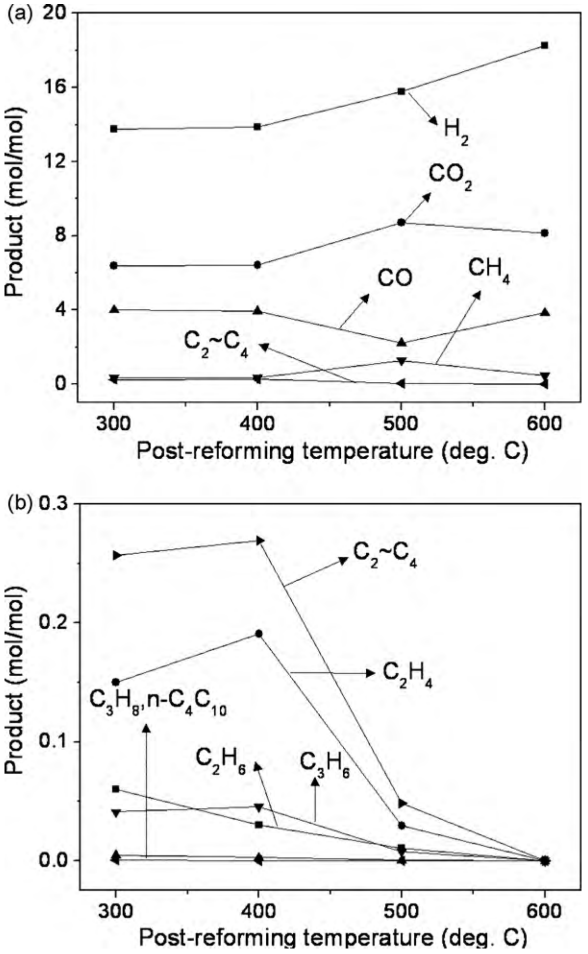

Fig. 8. Product distribution of post-reforming at several post-reforming temperatures. ATR catalyst (CGO-Pt (0.5 wt.%)) volume = 2 ml; GHSV = 12,500 h^{-1}; $H_2O/C = 2$; $O_2/C = 0.5$; ATR temperature = 800 °C; post-reforming catalyst (CGO-Ni (1.0 wt.%)) volume = 3.5 ml.

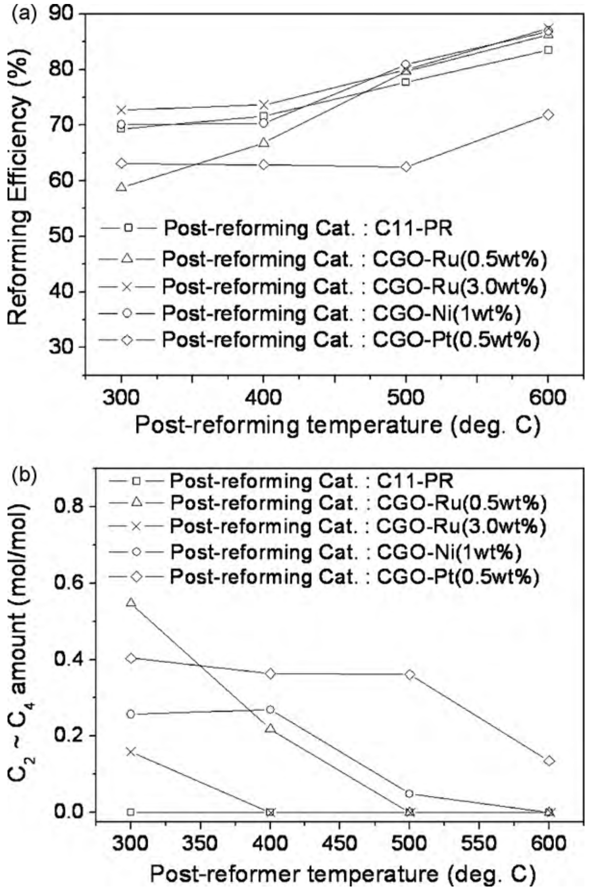

Fig. 9. (a) Reforming efficiency and (b) light hydrocarbon amounts in product gas vs. several post-reforming catalysts. ATR catalyst (CGO-Pt (0.5 wt.%)) volume = 2 ml; GHSV = 12,500 h^{-1}; $H_2O/C = 2$; $O_2/C = 0.5$; ATR temperature = 800 °C; post-reforming catalysts volume = 3.5 ml.

amounts of C_2H_4 and C_3H_6. The hydrogenation reaction of the light hydrocarbons (over C_1-hydrocarbons) with hydrogen is expressed in Eq. (6). In view of these results, we determined that the CGO-Pt catalyst is not suited for post-reforming because the light hydrocarbons (over C_1-hydrocarbons) in ATR reformate do not convert for the entire range of reforming temperatures.

$$C_nH_m + H_2 = C_nH_{m+2} \tag{6}$$

The CGO-Ru (0.5 wt.%) catalyst was also used for post-reforming, and Fig. 6 shows the amounts of the post-reforming products under various reforming temperatures. In case of using the CGO-Ru (0.5 wt.%) catalyst, the product distribution was different from when the C11-PR or CGO-Pt catalysts were used. For post-reforming temperatures of 500–600 °C, residual light hydrocarbons (over C_1-hydrocarbons) in the ATR reformate were completely converted. At 400 °C, residual light hydrocarbons (over C_1-hydrocarbons) were slightly converted, but the hydrogenation reaction occurred. At 600 °C, the product distribution was similar to that found when the C11-PR catalyst was used. This is because the WGS reaction dominated at this temperature. The CGO-Ru (0.5 wt.%) catalyst produced larger yields of H_2 and CO and smaller yields of CH_4 than the CGO-Pt (0.5 wt.%) catalyst at 500 °C. The difference in yields occurred because the methanation reaction was not a major contributor when the CGO-Ru (0.5 wt.%) catalyst was used. Moreover, at 300 °C, the ATR reformate was mostly unreacted, so most of the light hydrocarbons (over C_1-hydrocarbons) were not converted. Thus, to use the CGO-Ru catalyst for post-reforming, temperatures of post-reforming must be kept over 500 °C to completely remove the residual light hydrocarbons (over C_1-hydrocarbons).

Although the capacity of the CGO-Ru (0.5 wt.%) catalyst to remove the light hydrocarbons (over C_1-hydrocarbons) in the ATR reformate at temperatures up to 400 °C was lower than that for the C11-PR catalyst, but Ru-based catalysts does not need a hydrogen pre-reduction process for using catalyst. In addition, Ni-based catalysts have a lower coke tolerance than the Ru-based catalysts. We investigated the post-reforming characteristic using CGO-Ru (3.0 wt.%) because the activity of the CGO-Ru (0.5 wt.%) catalyst was lower than that of the C11-PR catalyst for removing the residual light hydrocarbons (over C_1-hydrocarbons).

Fig. 7 shows the amounts of post-reforming products under various temperatures with the CGO-Ru (3.0 wt.%) catalyst. Looking

Table 3
Conversion of light hydrocarbons (over C_1-hydrocarbons) in post-reforming vs. various catalysts.

Catalysts	Reaction temperature (°C)			
	300	400	500	600
C11-PR	100	100	100	100
CGO-Ni (1.0 wt.%)	59.23	57.26	92.36	100
CGO-Pt (0.5 wt.%)	35.88	42.3	42.73	78.61
CGO-Ru (0.5 wt.%)	12.95	65.44	100	100
CGO-Ru (3.0 wt.%)	74.89	100	100	100

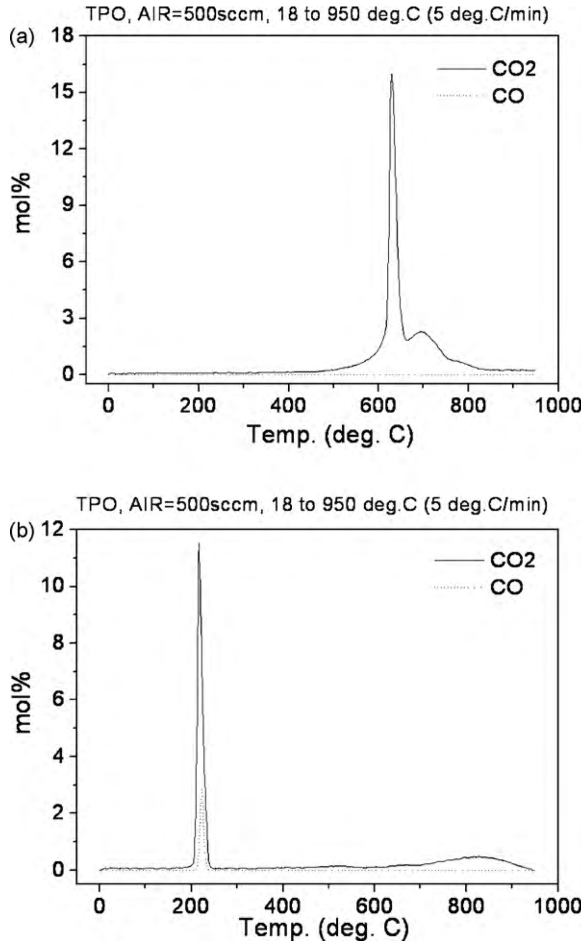

Fig. 10. Carbon detected by TPO after integrated reactions of ATR and post-reforming. ATR catalyst (CGO-Pt (0.5 wt.%)) volume = 2 ml; GHSV = 12,500 h^{-1}; $H_2O/C = 2$; $O_2/C = 0.5$; ATR temperature = 800 °C; post-reforming catalyst (C11-PR) volume = 2 ml; post-reforming temperature = 500 °C; (a) ATR reactor and (b) post-reforming reactor.

at the results, we found that light hydrocarbons (over C_1-hydrocarbons) in the ATR reformate were completely converted, and the CGO-Ru (3.0 wt.%) catalyst had a relatively smaller capacity for the methanation reaction than the C11-PR catalyst at temperatures greater than 400 °C. Actually, the residual light hydrocarbons (over C_1-hydrocarbons) were not completely converted into other products at 300 °C.

In the last catalyst screened, CGO-Ni (1.0 wt.%), was used for investigating the reaction characteristics of the Ni-based catalysts. The amounts of product gases are shown in Fig. 8. The CGO-Ni (1.0 wt.%) catalyst could not effectively convert the light hydrocarbons (over C_1-hydrocarbons) at temperatures up to and including 500 °C, which is different from the results of the C11-PR catalyst experiments. This difference is because much less Ni is contained in the C11-Ni catalyst than the C11-PR catalyst, resulting in a decrease in the activity of the catalyst. These phenomena are similar to those occurring in post-reforming experiments of the CGO-Ru catalysts.

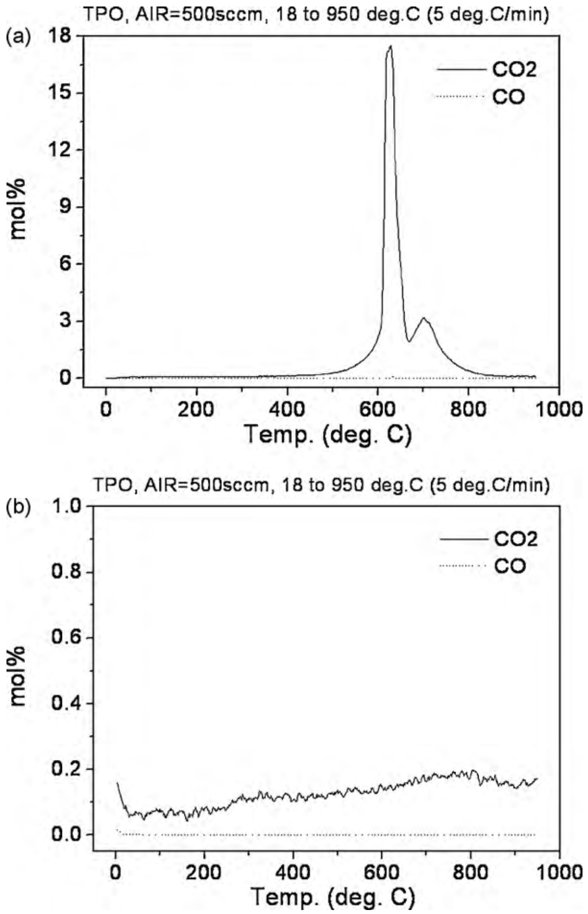

Fig. 11. Carbon detected by TPO after integrated reactions of ATR and post-reforming. ATR catalyst (CGO-Pt (0.5 wt.%)) volume = 2 ml; GHSV = 12,500 h^{-1}; $H_2O/C = 2$; $O_2/C = 0.5$; ATR temperature = 800 °C; post-reforming catalyst (CGO-Ru (0.5 wt.%)) volume = 2 ml; post-reforming temperature = 500 °C; (a) ATR reactor and (b) post-reforming reactor.

Fig. 9 shows the reforming efficiencies and the amounts of residual light hydrocarbons (over C_1-hydrocarbons) from the post-reforming reformate under several catalysts as functions of the post-reforming temperature. The CGO-Pt (0.5 wt.%) catalyst shows the worst performance, both in terms of the reforming efficiency and the conversion capacity of residual light hydrocarbons (over C_1-hydrocarbons). The conversions of light hydrocarbons (over C_1-hydrocarbons) in the post-reforming process for the various catalysts are listed in Table 3. In reforming efficiency, there is little difference between the C11-PR, CGO-Ni (1.0 wt.%), and CGO-Ru (3.0 wt.%) catalysts under all of the temperatures. However, the C11-PR catalyst shows the best performance for light hydrocarbon

Table 4
Catalyst summary for post-reforming.

	Catalysts	Post-reforming capability	Suitable temperature for post-reforming (°C)	Remarks
Ni-based catalysts	C11-PR	Very good	>300	Needs hydrogen reduction
	CGO-Ni (1.0 wt.%)	Well	>600	Low tolerance to carbon deposition
Noble metal-based catalysts	CGO-Pt (0.5 wt.%)	Bad	Impossible	Hydrogenation reaction of light hydrocarbons
	CGO-Ru (0.5 wt.%)	Well	>500	Needs Ru addition due to lower activity
	CGO-Ru (3.0 wt.%)	Very good	400	A suitable catalyst for post-reforming

removal. Comparing the C11-PR catalyst with the CGO-Ru (3.0 wt.%), we see that, although the light hydrocarbon removal by the CGO-Ru (3.0 wt.%) catalyst is worse at 300 °C, the CGO-Ru (3.0 wt.%) catalyst has higher reforming efficiency than the C11-PR catalyst at temperatures over 400 °C. This is because the C11-PR catalyst has a higher activity for the methanation reaction than the CGO-Ru (3.0 wt.%) catalyst in this temperature range, but the Ru-based catalyst does not need the hydrogen reduction protocol. In addition to that, the Ni-based catalysts have lower coke tolerance than noble metal-based catalysts. Actually, post-reforming reactors loaded with C11-PR and CGO-Ru (0.5 wt.%) catalysts were run for 60 h at the same conditions as for the integrated mode (ATR and post-reforming). After reaction, the deposited carbon in both the ATR and post-reforming reactors was analyzed by FT-IR using the TPO method, as shown in Figs. 10 and 11. The ATR TPO results of Figs. 10a and 11a show similar values of CO and CO_2. However, the TPO results of each post-reforming catalyst are different. The C11-PR post-reforming catalyst (Fig. 10b) produced much greater carbon levels than the CGO-Ru (Fig. 11b) catalyst. Light hydrocarbons (over C_1-hydrocarbons) were produced by the ATR reaction, and then the light hydrocarbons (over C_1-hydrocarbons) induced carbon deposition on the post-reforming catalyst, especially for the Ni-based catalyst.

After considering these results, we have determined that, if it is possible for the post-reforming temperature to remain over 400 °C, CGO-Ru (3.0 wt.%) is the best catalyst in this study. Characteristics of the post-reforming catalysts are summarized in Table 4. However, we still need a detailed analysis of post-reforming catalysts (Ni, Pt, and Ru catalysts) for understanding of different selectivity and activity of each catalyst. After this study, we would investigate the detained experiments for analysis of different catalysts characteristics in the post-reforming reaction.

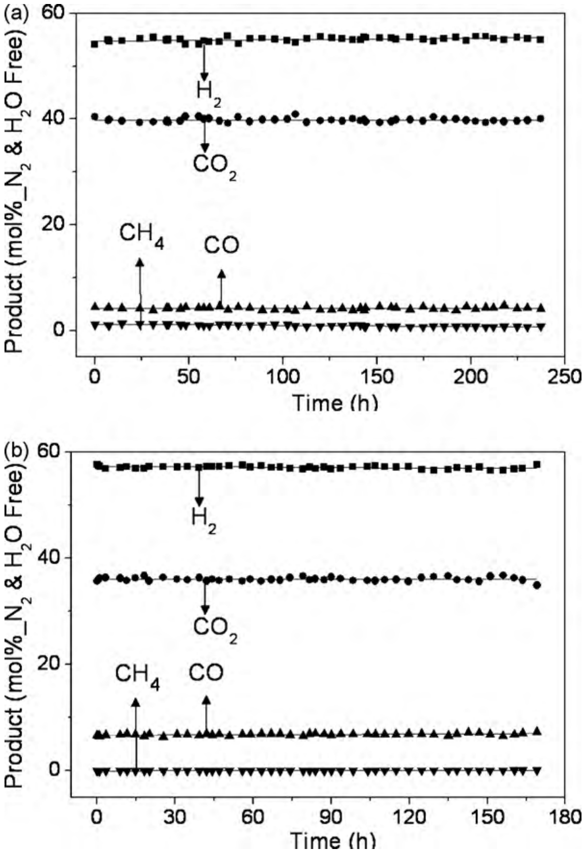

Fig. 12. Product distribution of post-reforming vs. operating time. ATR catalyst (CGO-Pt (0.5 wt.%)) volume = 1 ml; GHSV = 12,500 h^{-1}; $H_2O/C = 3$; $O_2/C = 0.8$; ATR temperature = 800 °C; post-reforming catalyst (CGO-Ru (3.0 wt.%)) volume = 1.75 ml; (a) post-reforming temperature = 500 °C and (b) post-reforming temperature = 600 °C.

Finally, long-term performance of commercial diesel fuel reforming was investigated using post-reforming with the CGO-Ru (3.0 wt.%) catalyst. The amounts of reformate products are shown in Fig. 12 for 500 °C and 600 °C post-reforming temperatures. The ATR temperature was fixed at 800 °C. Light hydrocarbons (over C_1-hydrocarbons) present in the product gas were not detected for about 200 h of operating time under both post-reforming temperatures. The product distribution was similar to that in the former experiments with CGO-Ru (3.0 wt.%).

In previous research, long-term performance of commercial diesel was guaranteed for about 250 h, but the amounts of light hydrocarbons (over C_1-hydrocarbons), especially C_2H_4, were dramatically higher in the ATR reformate. Hence, these experimental results emphasize the importance of the post-reforming methodology for completely removing the residual light hydrocarbons (over C_1-hydrocarbons) in the diesel ATR reformate.

4. Conclusion

In this paper, a new methodology called post-reforming is introduced for diesel reforming. To have stable operation of SOFCs, it is necessary to remove the light hydrocarbons (over C_1-hydrocarbons) in diesel reformate. Post-reforming can completely convert the light hydrocarbons (over C_1-hydrocarbons), carbon precursors on the SOFC anode, into H_2, CO and CO_2. Among the several catalyst candidates for post-reforming, the CGO-Ru (3.0 wt.%) catalyst shows the best performance, as it has a high capacity for light hydrocarbon removal and a high reforming efficiency. Although Ni-based catalysts also have a high capacity for light hydrocarbon removal, they show a lower reforming efficiency than Ru-based catalysts due to the dominant reaction path of methanation. The Ni-based catalysts even need the hydrogen reduction protocol. The Pt-based catalyst may not be used for post-reforming catalysts because the Pt catalyst aids in the hydrogenation reaction between olefins, such as C_2H_4 and C_2H_6, and H_2, in post-reforming. Using the CGO-Ru (3.0 wt.%) post-reforming catalyst, the diesel reforming system was continuously operated for about 200 h, and the light hydrocarbons (over C_1-hydrocarbons) were completely removed. In the case of applying the post-reforming methodology for diesel reforming, stable operation of the diesel-driven SOFC system is expected.

Acknowledgments

This work was funded by the Korea Electric Power Research Institute (KEPRI) and the KAIST EEWS Initiative. Analysis facilities, such as the GC–MS and SEM/EDX, were supported by the Ministry of Education and Human Resources Development.

References

[1] B.C.H. Steele, A. Heinzel, Nature 414 (2001) 345–352.
[2] J. Larminie, A. Dicks, Fuel Cell Systems Explained, 2nd ed., Wiley, New York, 2003 .
[3] K. Eguchi, H. Kojo, T. Takeguchi, R. Kikuchi, K. Sasaki, Solid State Ionics 152–153 (2002) 411–416.
[4] C.S. Subhash, K. Kevin, High Temperature Solid Oxide Fuel Cells, Elsevier Inc., New York, 2003.
[5] M. Boder, R. Dittmeyer, J. Power Sources 155 (2006) 13–22.
[6] S.H. Yoon, I.Y. Kang, J.M. Bae, Int. J. Hydrogen Energy 33 (2008) 4780–4788.
[7] P.K. Cheekatamarla, A.M. Lane, J. Power Sources 154 (2006) 223–231.
[8] A. Shamsi, J.P. Baltrus, J.J. Spivey, Appl. Catal. A: Gen. 293 (2005) 145–152.
[9] B. Lenz, T. Aicher, J. Power Sources 149 (2005) 44–52.
[10] I.Y. Kang, Y.H. Kang, S.H. Yoon, G.J. Bae, J.M. Bae, Int. J. Hydrogen Energy 33 (2008) 6298–6307.
[11] S.H. Yoon, I.Y. Kang, G.J. Bae, J.M. Bae, J. Korean Electrochem. Soc. 10 (2007) 110–115.

[12] J.R. Rostrup-Nielsen, T.S. Christensen, Ib Dybkjaer, Stud. Surf. Sci. Catal. 113 (1998) 81–95.
[13] T. Takeguchi, Y. Kani, T. Yano, R. Kikuchi, K. Eguchi, K. Tsujimoto, Y. Uchida, A. Ueno, K. Omoshiki, M. Aizawa, J. Power Sources 112 (2002) 588–595.
[14] A. Lindermeir, S. Kah, S. Kavurucu, M. Mühlner, Appl. Catal. B: Environ. 70 (2007) 488–497.
[15] J. Pasel, J. Meiβner, Z. Porš, R.C. Samsun, A. Tschauder, R. Peters, Int. J. Hydrogen Energy 32 (2007) 4847–4858.
[16] R.J. Farrauto, C.H. Bartholomew, Fundamentals of Industrial Catalytic Processes, 1st ed., Blackie Academic and Professional, London, 1997.
[17] X. Wang, R.J. Gorte, Appl. Catal. A: Gen. 224 (2002) 209–218.
[18] M. Krumpelt, T.-R. Krause, J.-D. Carter, J.-P. Kopasz, S. Ahmed, Catal. Today 77 (2002) 3–16.
[19] S.Y. Choung, M. Ferrandon, T. Krause, Catal. Today 99 (2005) 257–262.
[20] C11-PR adiabatic pre-reforming catalyst product bulletin, Süd-Chemie, pp. 1–11.
[21] J.H. Jeong, J.W. Lee, D.J. Seo, Y.T. Seo, W.L. Yoon, D.K. Lee, D.Y. Kim, Appl. Catal. A: Gen. 302 (2006) 151–156.
[22] S. Constantino, S. Michael, J. Catal. 93 (1985) 417–429.
[23] S.Y. Kim, S.H. Yoon, J.M. Bae, Y.S. Yoo, in: Proceedings of the ASME 7th International Fuel Cell Science Engineering and Technology Conference, 2009.