Autothermal reforming of propane over Ce modified Ni/LaAlO$_3$ perovskite-type catalysts

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ABSTRACT

In this study, Ce modified Ni/LaAlO$_3$ catalysts were prepared for propane autothermal reforming in order to increase the thermal catalyst stability and decrease the level of carbon deposition. In the Ce modified Ni/LaAlO$_3$ catalysts with different Ce loadings, the Ni-Ce/LaAlO$_3$ catalyst containing 5% Ce showed the highest reforming performance at high temperatures. Ce loading on the perovskite-type catalysts increased the thermal catalytic stability and decreased the level of carbon deposition during the autothermal reforming of propane. The influence of reaction temperature on the product showed that the CO concentration level could keep a low level when reformed at lower temperature. The propane autothermal reforming over the Ce modified perovskite-type catalysts showed high reforming performance due to the low carbon deposition on the catalyst surface.

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1. Introduction

Hydrogen is a pollution-free primary energy carrier for future transportation fuel and electricity generation because it has a high energy density and can be converted easily to electrical and thermal energy [1–4]. Depending on its applications, hydrogen can either be generated on-site or provided in storage tanks by liquefaction, gas compression, or other storage technologies. The hydrogen efficiency, system size, weight, start-up time, and life time, which are related to the temperature cycles and catalyst deactivation, should be considered for the cost-effective technology development for the on-site production of hydrogen requires [5]. Fuel process utilizing different hydrocarbons, such as methane, LPG (liquid propane gas) and gasoline, which have well-established distribution networks, is generally accepted as short- or mid-term solutions for the supply of hydrogen fuel [6–9].

Hydrocarbon reforming currently uses steam reforming, partial oxidation reforming, and autothermal reforming. Steam reforming is a highly endothermic process demanding an efficient heat supply to the system. This process is usually operated at high temperatures on Ni-based catalysts and a very energy- and capital-intensive process. It is considered to be an economically unattractive option, however, because it requires careful thermal management to provide enough heat for the reaction. On the other hand, partial

oxidation reforming provides the greatest fuel-type flexibility with an exothermal reaction using pure oxygen. However, it has disadvantages due to the lowest H$_2$ yield and high pollutant emissions, such as hydrocarbons and CO [10,11].

Autothermal reforming, taking the benefits of both steam reforming and partial oxidation, has recently attracted considerable attentions as one of the viable processes for hydrogen generation [12–14]. It offers advantages due to the small unit size and lower operational temperature, easier start-up, and wider choice of materials. In addition, it has higher energy efficiency than steam reforming and partial oxidation due to the low energy requirement, high GHSV (gas-hourly space velocity), lower process temperature, and easily regulated H$_2$/CO ratio by the inlet gas composition [15–18].

Current research efforts have focused on catalyst development in order to improve the activity, selectivity and stability under a realistic range of operating conditions. Decrease in the activity of the Ni-based alumina catalysts occurs due to carbon deposition during the hydrocarbon reforming. Therefore, the low-cost and long-proven performance of Ni-based catalysts warrants the efforts to optimize these catalysts in reforming applications [19].

Perovskite-type catalysts are considered to be one of the valuable alternatives to the supported noble metal catalysts for the catalytic hydrocarbon reforming because they are much cheaper, thermally stable and comparatively active [20,21]. Their general formula is ABO$_3$, where A is usually a rare earth cation (La, Gd, Pr, Nd, or Er) and B is a transition metal cation (Cr, Mn, Fe, Ni, Al, or Co). A-site replacement affects mainly the amount of sorbed

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oxygen, whereas B-site replacement influences the nature of the sorbed oxygen [22,23]. The partial substitution of the A cation with foreign cations with different oxidation states alters the oxidation state of the B-site cation and/or structural defects, such as anionic or cationic vacancies, in order to maintain the electroneutrality of the compound. In addition, the partial substitution of the B cation can improve both the structural stability and catalytic behaviors [24].

The hydrocarbon reforming results in the Ce-doped perovskite-type catalysts were rarely reported as far as we know. And, the temperature effect on the product composition including CO was seldom studied in autothermal reforming process using perovskite-type catalysts even though the control of the CO concentration is very important when reformed hydrogen is supplied to fuel cell systems.

In this study, the properties of the Ce modified perovskite-type catalysts were characterized in terms of the degree of carbon deposition and thermal stability. The propane reforming performances were evaluated by measuring the propane conversion and H_2 yield in a continuous fixed-bed reactor at reforming temperatures between 300 and 700 °C. In addition, the concentration profile of produced gases with the reaction temperature was analyzed for the CO concentration level.

2. Experimental

2.1. Preparation of catalysts

Perovskite-type $LaAlO_3$ catalysts for propane autothermal reforming were prepared using the citric acid sol–gel method [24]. That is, the required amount of $La(NO_3)_3 \cdot 6H_2O$ (Aldrich, USA), $Al(NO_3)_2 \cdot 9H_2O$ (Wako Pure, Japan) and citric acid (Wako Pure, Japan) were dissolved in ethylene glycol for the catalyst preparation. The resulting solution was heated slowly to 75 °C until a viscous gel was obtained. The gel was then evaporated to dryness and the obtained powder was calcined at 450 °C for 5 h in air.

The $Ni/LaAlO_3$ catalysts were prepared using four different methods, such as deposition–precipitation (DP) of Na_2CO_3 and NH_4OH, incipient wetness method, and dry impregnation method, and their performances were compared in the propane autothermal reforming. In addition, the Ce modified $Ni/LaAlO_3$ catalysts were prepared by mixing the calculated amounts of Ni and Ce nitrate with the diluted $LaAlO_3$ in distilled water. The supported catalysts were calcined at 450 °C for 5 h in air.

2.2. Characterization of catalysts

The powder X-ray diffraction (XRD) patterns of the perovskite catalysts were recorded on a Rigaku powder diffraction unit, DMAX 100, with mono-chromatized Cu Kα radiation. The diffraction patterns were identified by the comparison with the provided database. The temperature-programmed reduction (TPR) of the catalyst was performed at a ramping rate of 10 °C/min from ambient temperature to 500 °C using a 5 vol% H_2/Ar gas mixture as the reducing gas in a chemical analyzer, BEL-CAT (BEL, Japan). Thermal degradation of the catalysts was measured using a thermal gravimetric analyzer, TGA/SDTA 851^e (Mettler Toledo), in order to estimate the level of carbon deposition on the catalyst surface.

The morphology of the samples was examined by field emission scanning electron microscopy (FESEM, S-4700, Hitachi, Japan) at an accelerating voltage of 200 kV. The metal particle distribution of the catalysts was determined by transmission electron microscopy (TEM, JEN-2000FXII, JEOL, Japan) at an accelerating voltage of 200 kV. The pore properties (BET surface area, pore volume, and pore diameter) of the calcined catalysts were characterized using N_2 adsorption on an ASAP 2020 (Micromeritics, USA). The samples
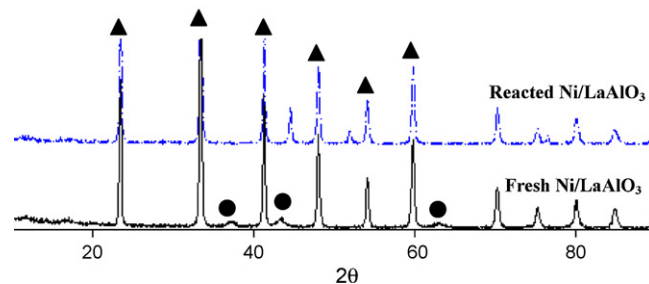

Fig. 1. Diffraction peaks for the $Ni/LaAlO_3$. $LaAlO_3$ (▲) and NiO (●).

were pre-treated in a N_2 atmosphere at 200 °C for 10 h before the measurements.

2.3. Evaluation of catalytic activity

The catalytic activity measurements were carried out in a continuous flow packed bed catalytic reactor at the atmospheric pressure. Five hundred milligrams of the catalyst was placed in a quartz glass tube with a 16 mm i.d. The temperature of the catalytic reactor was measured by a Cr-Al thermocouple. Steam was supplied by heating distilled water in a pre-heater during reforming. The experimental setup is found elsewhere for the propane autothermal reforming [25].

Before the reaction, the reactor circumstance was reduced by heating to 700 °C in 5 vol% H_2/N_2. The reaction tests for the catalyst activity were carried out using the following feed: $H_2O/C_3H_8 = 8.96$ and $C_3H_8/O_2 = 1.1$ at the GHSV of 9600 ml/(g-cat h). The reaction temperatures were varied from 300 to 700 °C. The gas species in the reaction products were analyzed on-line by gas chromatography (DS 6200, Donam, Korea) using Ar carrier gas with a thermal conductivity detector and columns packed with Porapak Q (2 m, 1/8 in i.d.) and 5A molecular sieves.

3. Results and discussion

3.1. Characterization of the perovskite-type catalysts

Fig. 1 shows the XRD patterns of the fresh and reacted Ni supported $LaAlO_3$ catalysts. The diffraction peak for NiO in the $Ni/LaAlO_3$ catalyst changed after propane reforming, while the $LaAlO_3$ peaks did not change even after reforming as shown in the figure. The XRD results indicate that $LaAlO_3$ has a stable structure.

The XRD peaks were compared with those from the $Ni/LaAlO_3$ catalysts prepared by different preparation methods. The crystalline structure of NiO changed according to the preparation method used. The crystallite size of NiO in the $Ni/LaAlO_3$ catalysts prepared by the different methods determined using the Scherrer equation was in the following order: Na_2CO_3 DP ($d = 8.96$ nm) < NH_4OH DP ($d = 11.17$ nm) < Incipient wetness ($d = 16.51$ nm) < Dry impregnation ($d = 25.65$ nm). The smaller crystalline size of NiO shows higher dispersion, thus increasing efficiency in the autothermal reforming of propane [26].

Table 1
BET adsorption results of the perovskite-type catalysts.

Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter[a] (nm)
$LaAlO_3$	3.6	0.05	54.5
$Ni(15)/LaAlO_3$[b]	15.4	0.11	28.2

[a] The pore diameter was determined by the BJH (Barrett–Joyner–Halenda) method.

[b] The number in parenthesis presents the Ni loading for catalyst preparation.
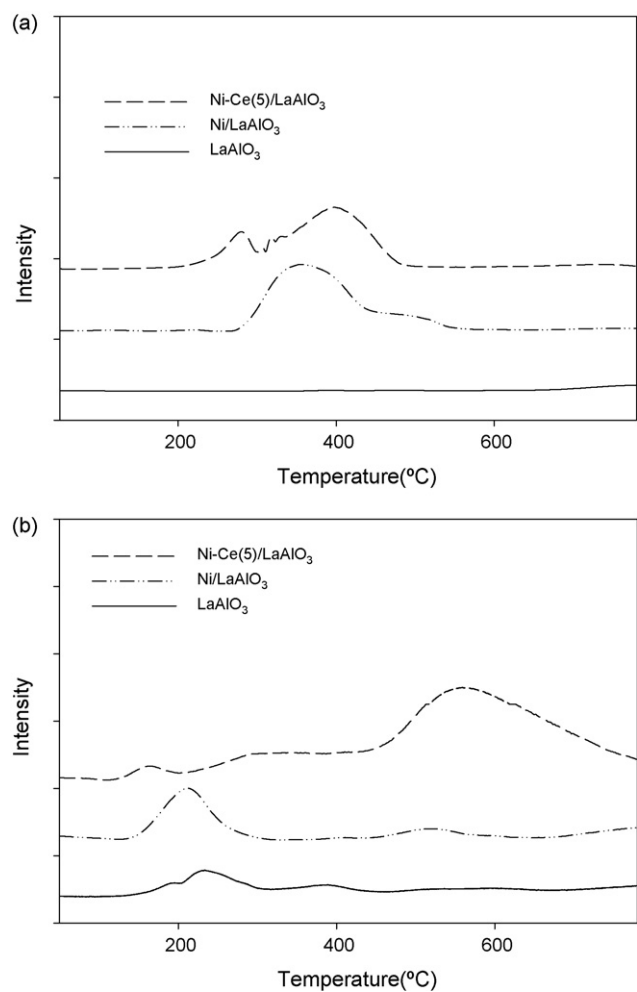
Fig. 2. TPR profiles for LaAlO₃, Ni/LaAlO₃ and Ni-Ce/LaAlO₃. (a) Before reaction and (b) after reaction.

The BET adsorption results for the Ni supported perovskite-type catalysts showed increasing BET surface areas and pore volumes compared with those for LaAlO₃, as shown in Table 1. The Ni loading increased the pore volume and BET surface approximately two and four times, respectively. However, the pore diameter decreased suggesting that the addition of Ni to the perovskite structure increased
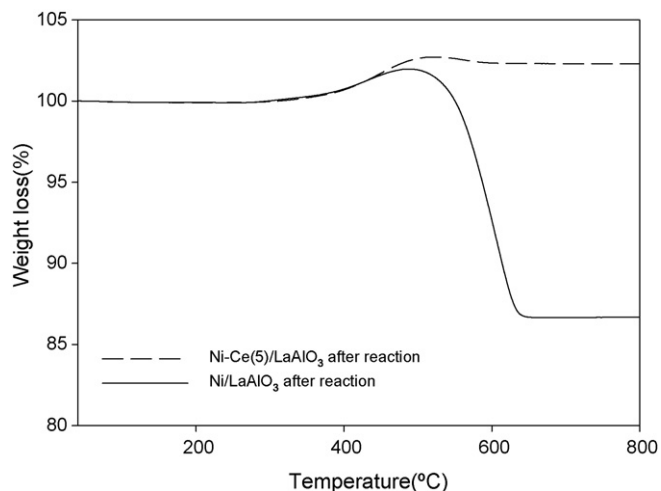

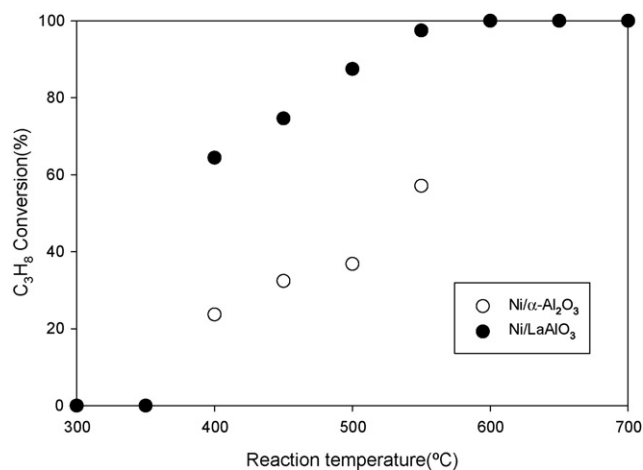Fig. 3. Measurement of thermal degradation for reacted catalysts.

Fig. 4. Influence of the Ni loading amount on the propane conversion (Ni loading amount: 15%).
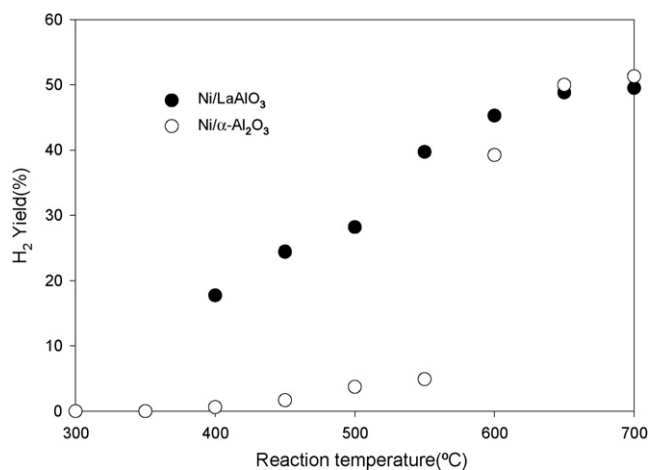

Fig. 5. Influence of the Ni loading amount on the H₂ yield (Ni loading amount: 15%).

the level of Ni dispersion [26]. The Ni in the perovskite catalyst may become more reducible than the LaAlO₃, leading to the formation of small particle on the surface and more abundant dispersion. It is suggested that the Ni particles facilitate the formation of coke residues, which encapsulate or cover metallic Ni particles, and hence the catalyst became deactivated [27].
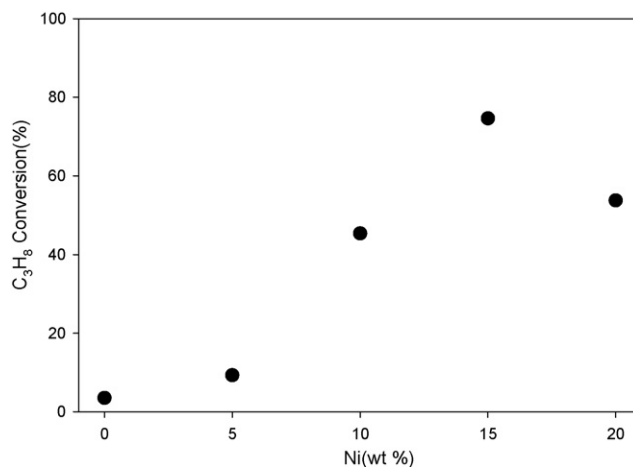

Fig. 6. Propane conversion as a function of the Ni loading amount at the reaction temperature of 450 °C.
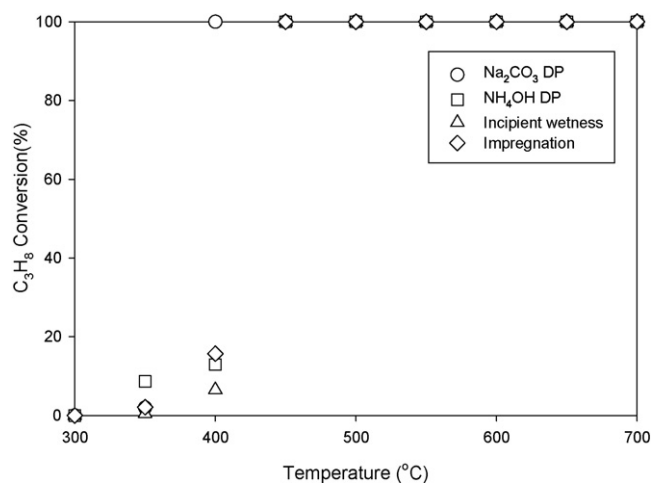
Fig. 7. Propane conversion for the Ni/LaAlO$_3$ catalysts prepared by four different methods.
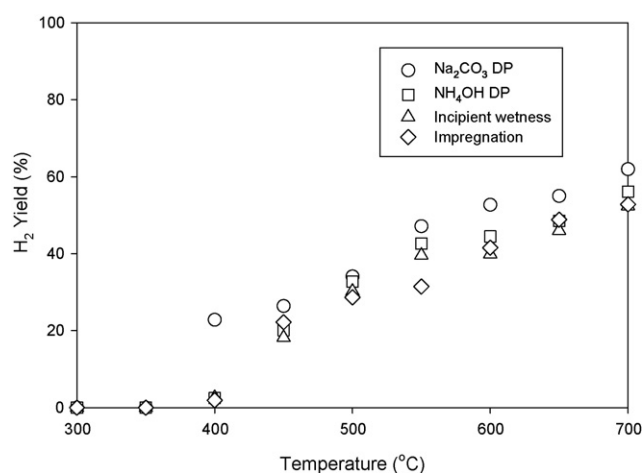

Fig. 10. H$_2$ yield for the Ni-Ce(x)/LaAlO$_3$ catalysts (x = 0, 0.2, 1, 5, 10%).

and reacted Ni/LaAlO$_3$ and Ni-Ce/LaAlO$_3$ catalysts showed that the catalysts surfaces showed little change even after reforming.

Fig. 2 shows the TPR profiles of the Ni/LaAlO$_3$ and Ni-Ce/LaAlO$_3$. In the case of Ni/LaAlO$_3$ in Fig. 2(a), the major peaks for the fresh catalyst were observed at approximately 400 and 500 °C. After reforming, a major new peak was observed at 210 and 560 °C in Fig. 2(b). In the TPR profile of the fresh Ni-Ce/LaAlO$_3$, the major peak

Fig. 8. H$_2$ yield for the Ni/LaAlO$_3$ catalysts prepared by four different methods.

3.2. Influence of reforming on the perovskite-type catalysts properties

In order to determine the influence of reforming on the catalysts, the catalyst surfaces of the Ni/LaAlO$_3$ and Ni-Ce/LaAlO$_3$ were analyzed by SEM after propane reforming. The SEM images of the fresh
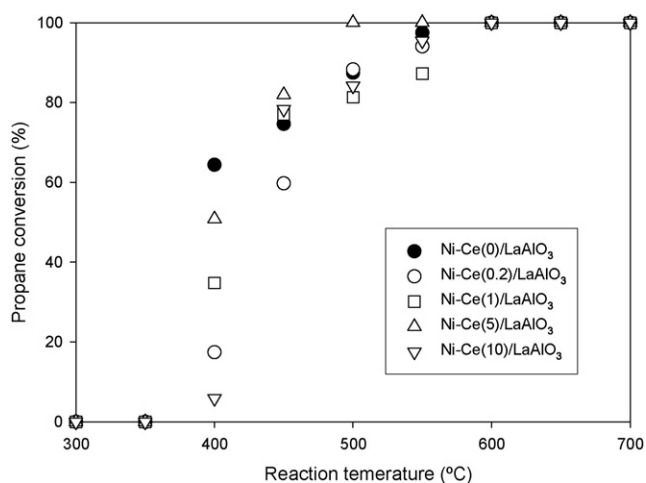

Fig. 9. Propane conversion for the Ni-Ce(x)/LaAlO$_3$ catalysts (x = 0, 0.2, 1, 5, 10%).
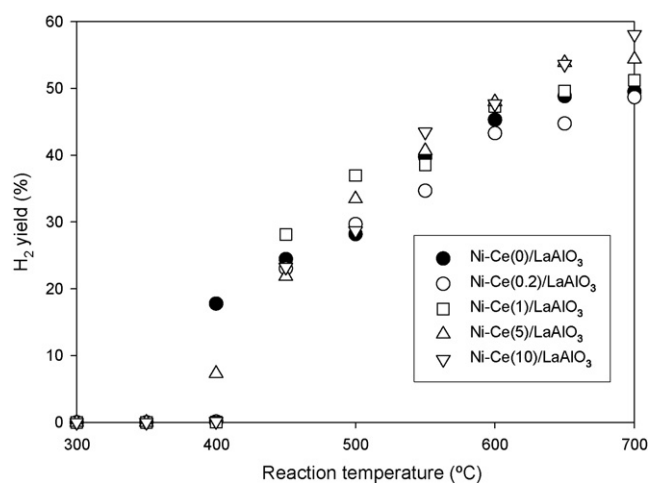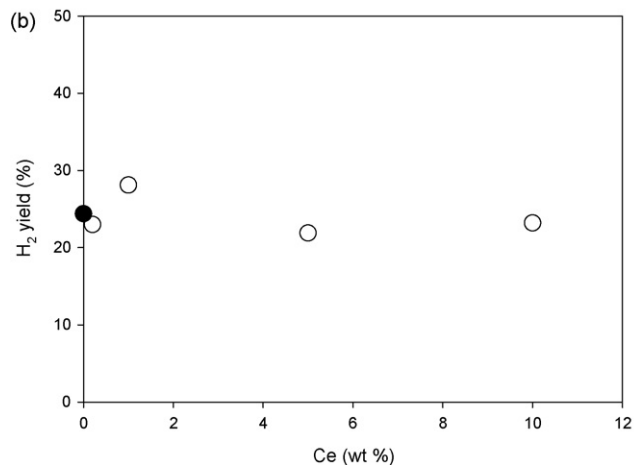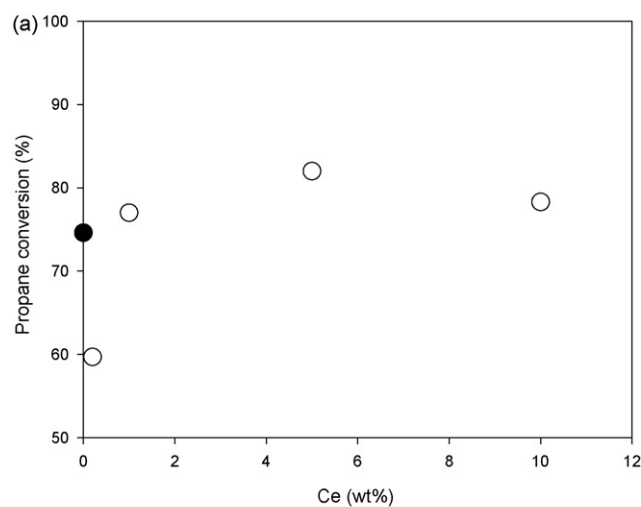

Fig. 11. Influence of the Ce loading amount on the propane reforming performances at the reaction temperature of 450 °C. (a) Propane conversion and (b) H$_2$ yield.
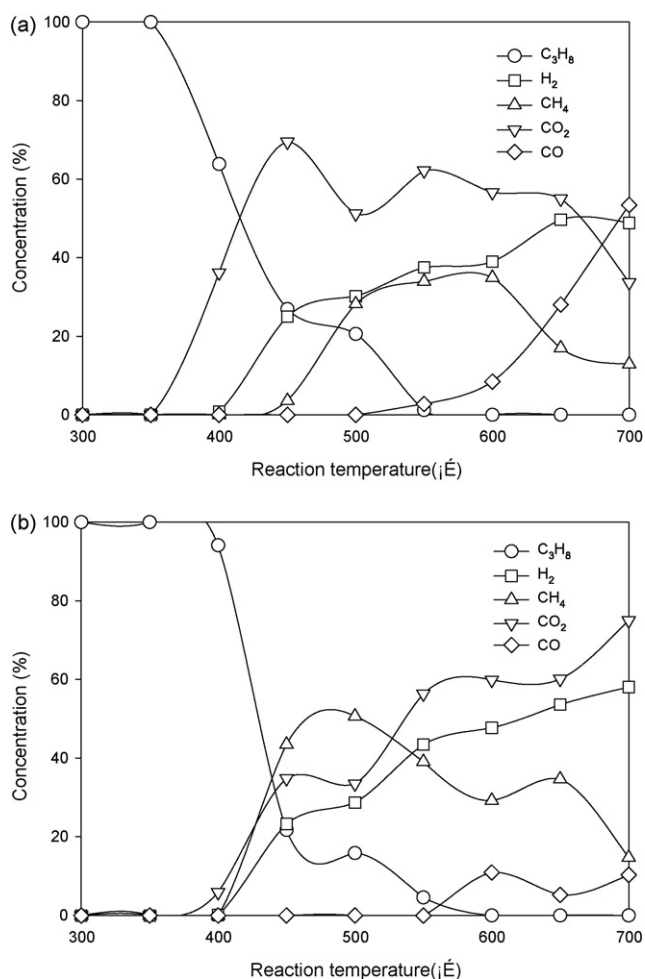
Fig. 12. Concentration profile of gas species in the product for the Ce modified Ni/LaAlO$_3$ catalyst. (a) Ni(15)-Ce(5)/LaAlO$_3$ and (b) Ni(15)-Ce(10)/LaAlO$_3$.

was observed at 410 °C shown in Fig. 2(a). This shift in the major peak compared with Ni/LaAlO$_3$ was attributed by the addition of Ce. The major peak in the reacted Ni-Ce/LaAlO$_3$ was observed at 580 °C with an additional peak at lower than 200 °C. The small peaks observed at approximately 200 °C may be related to physically deposited oxygen. Meanwhile, the major peaks at approximately 560–580 °C suggest that oxygen production decreases the level of carbon deposition and the catalyst activity.

Carbon deposition on the catalyst surface can be quantitatively analyzed by TGA. Fig. 3 shows the TGA results of the fresh and reacted Ni/LaAlO$_3$ and Ni-Ce(5)/LaAlO$_3$. Ni/LaAlO$_3$ began to degrade at 500 °C and its weight decreased by approximately 13% at temperature higher than 600 °C. Meanwhile, there was little decrease in the weight of the Ni-Ce/LaAlO$_3$, suggesting that the addition of Ce prevents carbon deposition during propane reforming.

3.3. Catalyst activity of the Ni/LaAlO$_3$ perovskite-type catalysts

The reforming efficiency of the Ni/LaAlO$_3$ catalyst prepared using the Na$_2$CO$_3$ DP method was compared with Ni supported on alumina (Ni/α-Al$_2$O$_3$) to determine the influence of the support on the propane reforming performances. The propane began to convert at approximately 350 °C for both catalysts, Ni/LaAlO$_3$ and Ni/α-Al$_2$O$_3$, as shown in Fig. 4. However, the perovskite-type catalyst showed a higher level of propane conversion at higher temperatures than 400 °C. At 400 °C, the level of propane conversion

on Ni/LaAlO$_3$ was 63%, which is much higher than that on the Ni/α-Al$_2$O$_3$. In addition, the H$_2$ yield on the perovskite catalyst was higher than that on the alumina support catalyst, as shown in Fig. 5. The H$_2$ yield increased linearly with temperature from 350 °C and reached approximately 40% at 700 °C. The Ni/α-Al$_2$O$_3$ showed notably lower H$_2$ yield. It is suggested that the more abundant Ni dispersion in the Ni/LaAlO$_3$ catalyst increase the catalytic activity. The Ni in the Ce-doped catalyst may lead formation of small particle on the surface since the aggregated Ni encapsulates or covers metallic Ni particles [28].

The level of propane conversion was measured at different reforming temperatures to determine the influence of the amount of deposited Ni on the reforming performance. Fig. 6 shows the level of propane conversion as a function of the amount of deposited Ni.
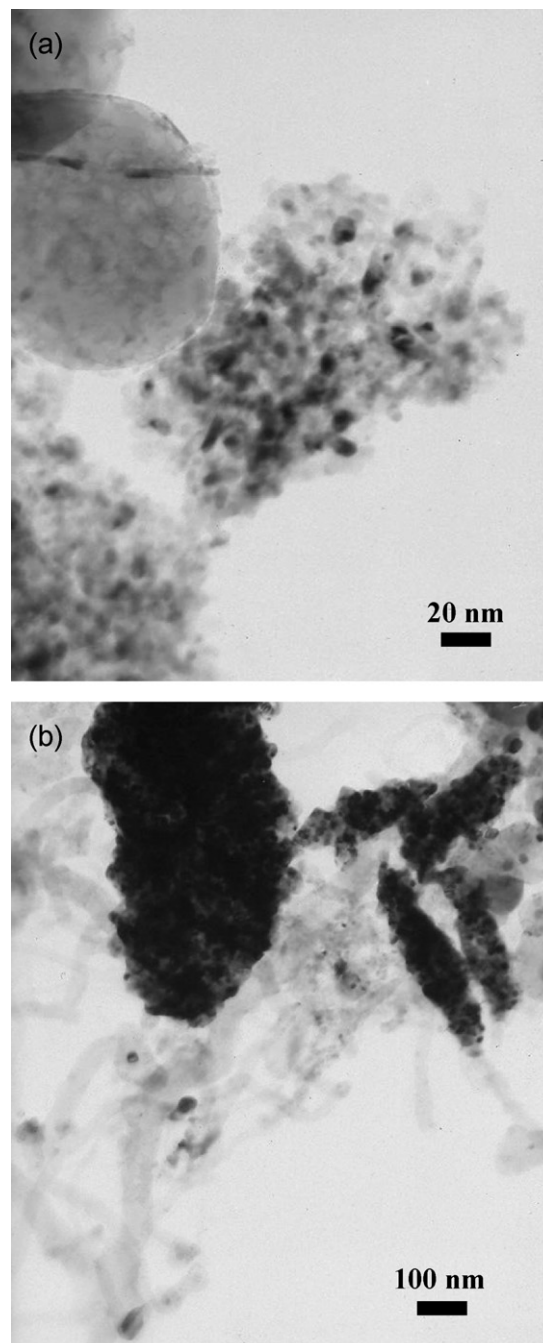

Fig. 13. TEM images for the perovskite-type catalysts (fresh Ni(15)-Ce(5)/LaAlO$_3$ (a) and reacted one (b)).

The level of propane conversion increased with increasing amount of Ni up to 15%. At higher amounts of Ni (20%), the conversion decreased for all reforming temperatures, as shown in the figure. It was observed that the Ni(15)/LaAlO$_3$ showed the highest reforming performance.

The influence of the preparation methods on the propane reforming performance was observed with Ni/LaAlO$_3$ catalysts prepared by four different methods. Fig. 7 shows the propane conversion on the different Ni/LaAlO$_3$ catalysts. As shown in the figure, the propane completely degraded at 450 °C for all four catalysts. However, the rates of propane conversion were different at lower reaction temperatures. The Ni/LaAlO$_3$ prepared by the NH$_4$OH DP, incipient wetness method, and dry impregnation method showed lower propane conversion than 20% at 400 °C, while the Ni/LaAlO$_3$ prepared by the Na$_2$CO$_3$ DP showed 100% propane conversion. The Ni/LaAlO$_3$ prepared by the Na$_2$CO$_3$ DP showed the highest H$_2$ yield in Fig. 8. The H$_2$ yield of the Na$_2$CO$_3$ DP was slightly higher than the others. It is considered that the higher reforming efficiency in the Ni/LaAlO$_3$ prepared by the Na$_2$CO$_3$ DP is related to the higher dispersion due to the smaller crystalline size [13,14].

3.4. Catalyst activity of the Ni-Ce/LaAlO$_3$ perovskite-type catalysts

The Ni(15)-Ce/LaAlO$_3$ catalysts were prepared by the deposition–precipitation of Na$_2$CO$_3$ at different Ce concentrations to investigate the influence of the deposited amount on the reforming performance. Fig. 9 shows the level of propane conversion on Ni-Ce(x)/LaAlO$_3$ (x = 0, 0.2, 1, 5, 10%). As shown in the figure, the propane conversion level of the Ce modified catalysts was lower than that of Ni-Ce(0)/LaAlO$_3$, which may be related to the lower amount of Ni on the catalysts. At higher temperatures than 400 °C, the Ni-Ce(5)/LaAlO$_3$ showed the highest propane conversion. In terms of the H$_2$ yield, the Ni-Ce(x)/LaAlO$_3$ catalysts showed similar or higher values compared with Ni-Ce(0)/LaAlO$_3$ (see Fig. 10). The H$_2$ yield of the Ni-Ce(x)/LaAlO$_3$ showed somewhat higher values except Ni-Ce(0.2)/LaAlO$_3$ at high temperatures even though the value were lower values than that of the Ni-Ce(0)/LaAlO$_3$ at the lower temperature than 400 °C. It is considered that the noble metal doping increased the degree of Ni dispersion, thus decreasing level of carbon on the catalyst surface.

Fig. 11 shows the influence of the Ce concentration on the reforming performances. The Ni-Ce/LaAlO$_3$ with the lowest Ce concentration showed 60% conversion shown in Fig. 11(a). The level of propane conversion increased with increasing Ce concentration, showing a similar value of approximately 80%. The level of propane conversion for the Ce modified Ni/LaAlO$_3$ catalysts were higher than on the Ni-Ce(0)/LaAlO$_3$ catalyst. The H$_2$ yield shown in Fig. 11(b) was not significantly changed with increasing Ce concentration.

The result implies that Ce modification affects the level of propane conversion rather than the H$_2$ yield.

It is of importance to maintain low level of CO concentration in reforming systems because CO can poison the Pd catalyst in the membrane-electrode assembly (MEA) of a fuel cell stack [29]. In this study, the CO concentration level in the products was checked with the on-line GC analysis system. Fig. 12 shows the concentration of each gas species as a function of the reaction temperature. The concentration profile for the Ni(15)-Ce(5)/LaAlO$_3$ in Fig. 12(a) shows that propane degradation began at approximately 400 °C with 35% propane degradation. At higher temperature than 550 °C, the propane completely degraded. The H$_2$ concentration increased linearly with temperature. In the case of CO$_2$ and CH$_4$, the concentration increased at the lower temperature and decreased at higher temperatures than 500 °C. Considering the CO profile, the concentration increased significantly at higher temperature than 600 °C.

Fig. 12(b) shows the concentration profile of Ni(15)-Ce(10)/LaAlO$_3$. The results were similar to those of the Ni(15)-Ce(10)/LaAlO$_3$ except for CO$_2$ and CO. The CO$_2$ concentration in the Ni(15)-Ce(10)/LaAlO$_3$ catalyst increased linearly up to 76%. Interestingly, the CO profile linearly increased, the measured concentration being 12% at 700 °C. In addition, the CO concentration was significantly lower at 550 °C, similar to the result of Ni(15)-Ce(5)/LaAlO$_3$. Based on the concentration profile with the reaction temperature, it is suggested that reforming on the Ce modified catalysts should be performed at lower temperatures than 550 °C in order to decrease the amount of produced CO.

Fig. 13 shows TEM images of the fresh and reacted Ni-Ce/LaAlO$_3$. In the fresh catalyst, the particle sizes of the distributed catalysts on the surface of Ni-Ce/LaAlO$_3$ were measured to be 10–15 nm in Fig. 13(a). Fig. 13(b) shows that the carbon deposited as a fiber type deposit after propane reforming. It is known that carbon deposits in the form of graphite significantly affect the activity, while the fiber type deposition has little effect on the catalyst activity [30]. It is considered that the catalyst activity was little affected due to a low amount of deposited carbon with a fiber type on the surface.

The performance of the propane autothermal reforming over the perovskite-type catalysts were compared with the reported results and the data are presented in Table 2. The Au modified La$_{0.59}$Sr$_{0.41}$MnO$_3$ increased the level of propane conversion and the H$_2$ yield compared to La$_{0.59}$Sr$_{0.41}$MnO$_3$ [21]. Also, the Ni and Ce modification showed the increasing propane reforming performance compared to LaAlO$_3$. The noble metal modified perovskite-type catalysts showed significantly higher propane performance compared with the reforming results of the Au modification. It is noted that the Ce modified perovskite-type catalysts showed high performance due to the Ni particle dispersion and the low carbon deposition on the catalyst surface.

Table 2
Performance of the propane autothermal reforming over the perovskite-type catalysts.

Composition of catalysts	Catalyst preparation	Reforming conditions	Propane reforming at 600 °C	References
La$_{0.59}$Sr$_{0.41}$MnO$_3$	Sol–gel	• 600–800 °C • H$_2$O/C = 0.83, O/C = 0.5 • GHSV: 60,000 l/h	• Conversion: 41% • H$_2$ yield: 5%	[21]
Au(5)/La$_{0.59}$Sr$_{0.41}$MnO$_3$	Sol–gel	• 600–800 °C • H$_2$O/C = 0.83, O/C = 0.5 • GHSV: 60,000 l/h	• Conversion: 82% • H$_2$ yield: 32%	[21]
LaAlO$_3$	Sol–gel	• 300–700 °C • H$_2$O/C/O = 3/1/0.37 • GHSV: 9600 ml/g-cat h	• Conversion: 69% • H$_2$ yield: 5%	[26]
Ni(15)-Ce(5)/LaAlO$_3$	Sol–gel/DP	• 300–700 °C • H$_2$O/C/O = 3/1/0.37 • GHSV: 9600 ml/g-cat h	• Conversion: 100% • H$_2$ yield: 41%	This study

4. Conclusions

Carbon deposition on the catalyst surface and the catalyst stability are considered to be serious problems in the production of hydrogen in autothermal reforming. In this study, $Ni/LaAlO_3$ and $Ni-Ce/LaAlO_3$ catalysts were prepared mainly by the deposition–precipitation of Na_2CO_3 and subsequent calcination in air. The catalyst activities were tested in a quartz reactor with a reactant ratio of $H_2O/C_3H_8/O_2 = 8.96/1.0/1.1$ at a velocity of 9600 ml/g-cat h. The highest propane conversion was observed on the $Ni/LaAlO_3$ catalyst containing 15% Ni at reforming temperatures ranging from 300 to 700 °C.

The Ce loading in perovskite-type catalysts increased thermal stability weight change in the TGA results, implying that the addition of Ce suppressed the carbon deposition during the propane reforming. The carbon fiber type of the deposited carbon suggests that it has a low effect on the $Ni/LaAlO_3$ catalyst activity. The concentration profile of produced gases with the reaction temperature suggests that reforming on the Ce modified catalysts should be performed at lower temperatures than 550 °C in order to minimize the level of CO production. Overall, the Ce modified perovskite-type catalysts showed high performance, good thermal stability due to the Ni particle dispersion and the low carbon deposition on the catalyst surface.

Acknowledgements

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