

Effect of CeO₂-addition sequence on the performance of CeO₂-modified Ni/Al₂O₃ catalyst in autothermal reforming of iso-octane

Sang Ok Choi, In Young Ahn, and Sang Heup Moon[†]

School of Chemical & Biological Engineering and Institute of Chemical Processes,
Seoul National University, San 56-1, Shillim-dong, Kwanak-gu, Seoul 151-744, Korea
(Received 24 February 2009 • accepted 13 March 2009)

Abstract—Two types of CeO₂-modified Ni/Al₂O₃ catalysts were prepared by a consecutive impregnation method with different sequences in the impregnation of Ni and CeO₂, and their performance in autothermal reforming (ATR) of iso-octane was investigated. Catalysts prepared by adding CeO₂ prior to the addition of Ni, Ni/CeO₂-Al₂O₃, produced larger amounts of hydrogen than those obtained using catalysts prepared by adding the two components in an opposite sequence, Ni-CeO₂/Al₂O₃. The results of H₂ chemisorption and temperature-programmed reduction revealed that added CeO₂ increased the dispersion of the Ni species on Al₂O₃ and suppressed the formation of NiAl₂O₄ in the catalyst such that large amounts of Ni species were present as NiO, the active species for the ATR. The elemental and thermogravimetric analyses of deactivated catalysts indicated that Ni/CeO₂-Al₂O₃, which showed a longer lifetime than Ni-CeO₂/Al₂O₃, contained lesser amounts and different types of coke on the surface.

Key words: Autothermal Reforming, Steam Reforming, Hydrogen Production, CeO₂, Iso-octane

INTRODUCTION

Autothermal reforming (ATR), in which heat required for the endothermic reforming reaction is supplied by the partial oxidation of feed hydrocarbons, is considered as one of the promising processes for producing hydrogen. Numerous studies have been done to develop improved catalysts for ATR [1-9], but most of them are focused on processes using relatively light hydrocarbons such as methane [2-6], methanol [7,8] and ethanol [9]. The ATR of gasoline is recently considered as an alternative [10,11] because it has the advantage of using the current infrastructure of gas stations.

Even though Ni/Al₂O₃, a commercial catalyst for the steam reforming of CH₄, also shows a high activity for gasoline ATR, it is easily deactivated by coke produced in the process and accordingly the catalyst lifetime is short [12,13]. In this respect, it is a key issue in gasoline ATR to design a catalyst that allows the production of minimum amounts of coke.

Many additives, including alkali metals (Na, K) [14], alkali earth metals (Mg, Ca) [15,16] and Mo [17], were proposed as promoters of the Ni catalyst for suppressing the formation of coke in reforming. However, one of drawbacks of these promoters was that they simultaneously decreased the activities of the original catalysts [14, 17]. Unlike the above cases, it was reported that the initial activity was not decreased when CeO₂ was used as a promoter of reforming catalysts [18]. For example, Wang et al. [19] reported that the addition of CeO₂ into Ni/Al₂O₃ systems not only increased the catalytic activity and stability but also suppressed the carbon deposition. Feio et al. [20] suggested that the above effect of CeO₂ originated from its 1) high oxygen storage capacity, which promoted the gasification of coke and consequently decreased the amounts of de-

posited coke, and 2) contribution to metal dispersion, which increased the number of active sites in the catalyst. Accordingly, we have selected CeO₂ as a candidate promoter of the Ni catalyst for the reforming of gasoline, which is subject to severe deactivation by coking [18-20].

CeO₂-promoted Ni catalysts can be prepared by two different methods depending on the sequence of adding Ni and CeO₂: 1) by adding Ni prior to CeO₂ addition, and 2) by adding the two components in an opposite sequence. Sequence 1) will maximize the exposed surface area of added CeO₂ and consequently the gasification of coke in the catalyst. On the other hand, sequence 2) will maximize the contribution of CeO₂ to the dispersion of Ni on the support as a result of increased CeO₂-Ni interaction.

Cheng et al. [21] reported that the promotional effect of lanthanide oxides, e.g., La₂O₃ and CeO₂, in CO₂ reforming of methane was not sensitive to the preparation procedure such as co-impregnation or consecutive impregnation. On the other hand, it was reported that the introduction sequence of Rh and La₂O₃, consecutive or co-impregnation, affected the catalytic activity of Rh/La₂O₃/SiO₂ in benzene hydrogenation and n-butane hydrogenolysis reactions [22]. The above results suggest that the catalyst performance can be influenced to different extents by the sequence of introducing the promoter and the active metal component according to the specific cases of catalysts and catalytic reactions.

In this paper, the performance of CeO₂-added Ni catalysts in the ATR of iso-octane, a model compound representing gasoline, was investigated. To observe the effect of the sequence of metal addition, two types of CeO₂-modified Ni/Al₂O₃ catalysts were prepared by changing the sequence of Ni and CeO₂ addition. The prepared catalysts were tested in iso-octane ATR and characterized by N₂-physisorption, H₂-chemisorption and temperature-programmed reduction (TPR). The amounts and the species of coke formed on the catalysts during the reaction were investigated by elemental (EA)

[†]To whom correspondence should be addressed.
E-mail: shmoon@surf.snu.ac.kr

and thermogravimetric analyses (TGA).

EXPERIMENTAL

1. Catalyst Preparation

γ -Al₂O₃ obtained from CONDEA (surface area=206.6 m²/g, pore volume=0.48 cm³/g) was crushed into 60-80 mesh (180-250 μ m) powders and dried at 110 °C overnight. CeO₂-modified Ni/Al₂O₃ catalysts were prepared by impregnating the γ -Al₂O₃ with an aqueous solution containing Ni(NO₃)₂·6H₂O and Ce(NO₃)₃·6H₂O. The prepared catalysts were designated as Ni/CeX or Ni-CeX, 'X' denoting the amount of added CeO₂ in wt%, according to whether they were prepared by adding CeO₂ prior to Ni addition or in the reverse sequence, respectively. The NiO loading was fixed at 5 wt%, but the amounts of added CeO₂ varied between 2 and 20 wt%. Prepared catalysts were dried in air at 110 °C overnight and finally calcined in air at 500 °C for 5 h.

2. Characterization

The BET surface areas and the average pore sizes of the Al₂O₃ support and the metal loaded catalysts were measured by N₂ physisorption using ASAP2010 (Micromeritics). Prior to the measurements, the cell containing the sample catalyst was evacuated at 200 °C for 1 h to remove impurities and water adsorbed on the surface.

The temperature-programmed reduction (TPR) of the catalysts, Ni-CeX, Ni/CeX and Ni/Al₂O₃, was performed to investigate their reduction properties. Prior to the TPR, the sample catalyst was heated

in He at 120 °C for 1 h to remove water from the surface. The TPR experiment was conducted by raising the temperature from 30 °C to 900 °C at a rate of 5 °C/min in a 5 mol% H₂/Ar stream flowing at 30 ml/min. Changes in the H₂ concentration of the effluent stream were monitored with a gas chromatograph (Younglin, M600D) equipped with a thermal conductivity detector (TCD).

The dispersion of Ni in Ni-CeO₄, Ni/CeO₆, and Ni/Al₂O₃ was measured by H₂ chemisorption using ASAP 2010 from Micromeritics. Prior to the measurements, the sample catalyst was reduced in H₂ at 700 °C for 1 h and vacuum-treated at the same temperature for 10 min. Finally, the cell containing the sample catalyst was purged in flowing He prior to evacuation for 10 min. The initial isotherm was obtained at 35 °C over the pressure range of 20-100 Torr. The cell was evacuated for 30 min prior to measuring the second isotherm.

3. Iso-octane ATR

A schematic diagram of the iso-octane ATR system used in this study is shown in Fig. 1. H₂O (distilled water), air (99.999%) and 2,2,4-trimethyl pentane (iso-octane, Aldrich, 99.8%) were used as reactants for the ATR. The flow rates of H₂O and iso-octane were controlled by syringe pumps (KDS-200) and the flow rate of air by a mass flow controller (Unit, 8100). The liquid reactants, H₂O and iso-octane were vaporized in the evaporator maintained at 180 °C, prior to being mixed with air. The mixed reactants were introduced into the U-shaped quartz reactor containing the sample catalyst through a stainless tube line maintained at 120 °C. The temperature of the

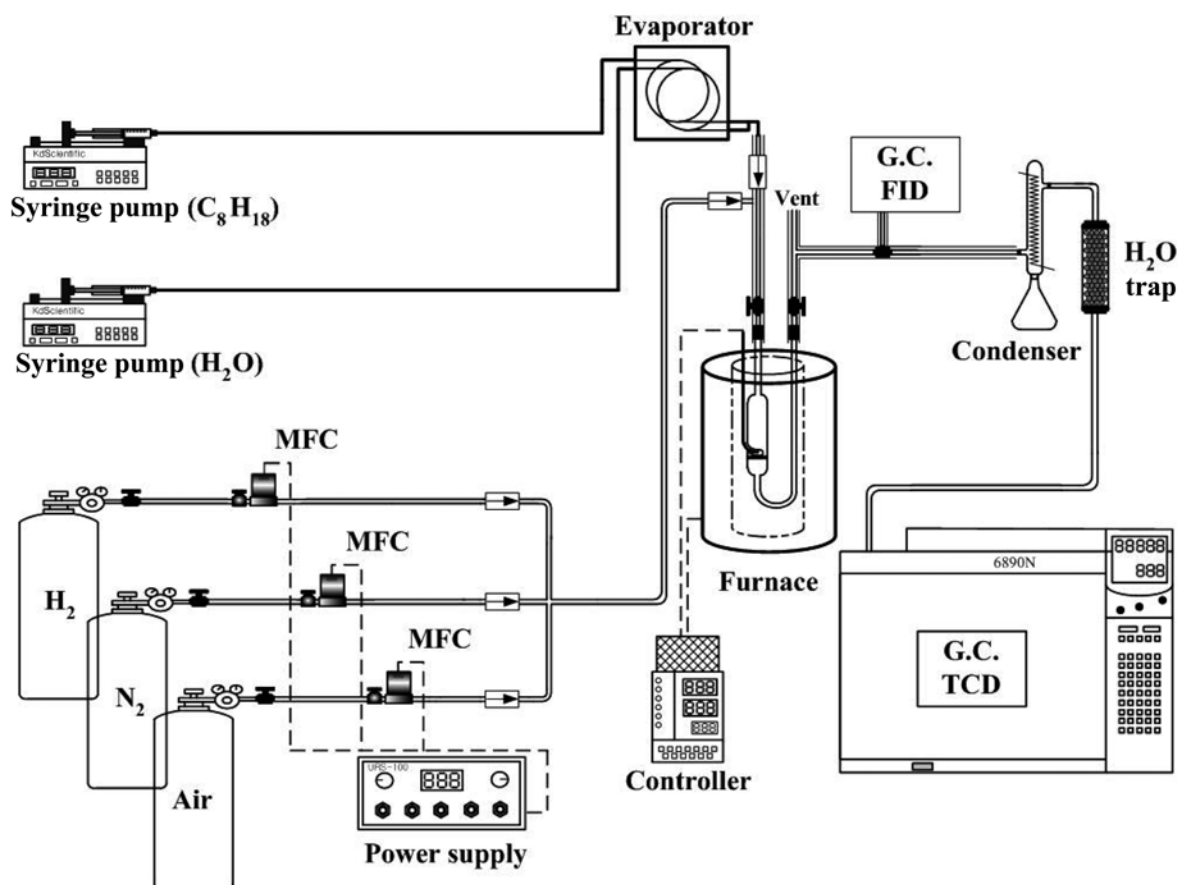


Fig. 1. Schematic diagram of iso-octane ATR system.

sample catalyst was measured and controlled by a K-type thermocouple and an electric furnace, respectively. Products in the effluent stream were analyzed by two gas chromatographs: HP model 6890 equipped with a TCD and a Carbosieve II column for analyzing H_2O , CO , CO_2 and CH_4 ; HP model 5890 equipped with an FID and a HP-1 column for analyzing hydrocarbons.

Prior to the iso-octane ATR, the sample catalyst was reduced at 700°C in H_2/N_2 for 1 h and the catalyst temperature was lowered to 600°C in N_2 . The mixed reactants were introduced into the reactor after the flow reached a steady state. The $\text{H}_2\text{O}/\text{C}/\text{O}$ ratio was maintained at 3/3/0.25 and the total flow rate at 68.8 ml/min.

4. Coke Analysis

The amounts of coke deposited on the catalyst after reaction for 48 h were determined by elemental analysis (EA, CE Instrument). The coke species were analyzed thermogravimetrically (TGA, Rubotherm), while the sample temperature was raised from 30°C to 700°C at a rate of $10^\circ\text{C}/\text{min}$ in 10 mol% O_2/N_2 flowing at 30 ml/min.

RESULTS

1. Catalyst Characterization

The textual properties, including BET surface area, average pore diameter and Ni dispersion, of CeO_2 -modified and unpromoted $\text{Ni}/\text{Al}_2\text{O}_3$ are shown in Table 1. The BET surface area of the catalyst, which was $195.0\text{ m}^2/\text{g}$ for unpromoted $\text{Ni}/\text{Al}_2\text{O}_3$, decreased with an increase in the CeO_2 loading regardless of the CeO_2 -impregnation sequence. The average pore diameters of the catalysts were nearly the same except when the catalysts contained 20 wt% of CeO_2 , i.e., Ni-Ce20 and Ni/Ce20 . Ni/Ce06 showed the highest Ni dispersion, 7.1%, whereas $\text{Ni}/\text{Al}_2\text{O}_3$ and Ni-Ce04 showed relatively low Ni dispersions, 5.5% and 2.3%.

The TPR of the catalysts (Fig. 2) shows four kinds of peaks. Peak 1 appearing at temperatures below 450°C , which is not observed in the case of unpromoted $\text{Ni}/\text{Al}_2\text{O}_3$, increases in intensity with an increase in the amounts of added CeO_2 and therefore originates from the reduction of CeO_2 [23]. Peaks 2 and 3, which are observed in the temperature range of $450\text{--}700^\circ\text{C}$ and at about 800°C , represent

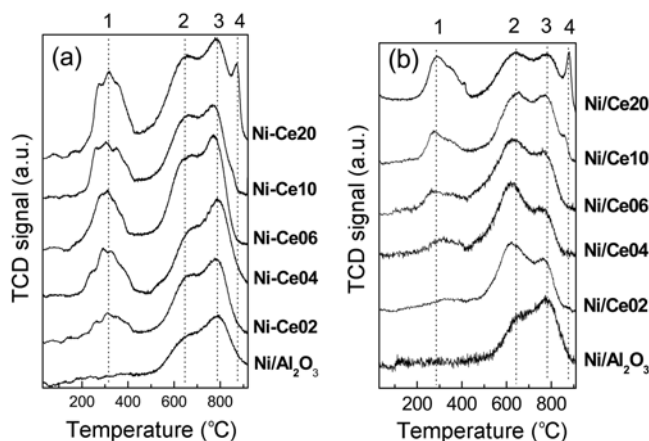


Fig. 2. TPR profiles for (a) Ni-CeX and (b) Ni/CeX .

Table 2. Peak area calculated by peak deconvolution from TPR result

Catalyst	Peak 2 area ^a	Peak 3 area ^b	a/(a+b)
$\text{Ni}/\text{Al}_2\text{O}_3$	72	115	0.39
Ni-Ce04	127	143	0.47
Ni/Ce06	252	44	0.85

the reduction of NiO and NiAl_2O_4 , respectively [21]. A separate TPR experiment made with a sample containing only CeO_2 (not shown) indicated that CeO_2 was reduced at temperatures higher than 850°C . Accordingly, peak 4, which is observed at about 870°C in Fig. 2, is supposed to represent the reduction of isolated CeO_2 , which will be presented in a significant amount when the catalyst is loaded with 20 wt% CeO_2 .

In the case of unpromoted $\text{Ni}/\text{Al}_2\text{O}_3$, the area of peak 3 was larger than that of peak 2, indicating that a larger amount of the Ni species was present as NiAl_2O_4 instead of NiO . The TPR results of Ni-CeX showed the same trend as $\text{Ni}/\text{Al}_2\text{O}_3$. However, in the case of Ni/CeX , an opposite trend was observed, i.e., a larger amount of Ni existed as NiO instead of NiAl_2O_4 . The areas of peak 2 and peak 3 were estimated after deconvolution of the peaks and summarized in Table 2. The order of the peak area ratio, peak 2/(peak 2+peak 3), was $\text{Ni/Ce06} > \text{Ni-Ce04} > \text{Ni}/\text{Al}_2\text{O}_3$.

2. Activities of Ni-CeX and Ni/CeX

The amounts of produced hydrogen, which are normalized to the initial amount of hydrogen obtained using $\text{Ni}/\text{Al}_2\text{O}_3$, are shown in Fig. 3 for Ni-CeX and Ni/CeX catalysts. In the case of Ni-CeX , the initial amounts of produced hydrogen were nearly the same or slightly higher than that obtained using $\text{Ni}/\text{Al}_2\text{O}_3$. On the other hand, the amounts of hydrogen obtained with Ni/CeX catalysts were larger than in the case of $\text{Ni}/\text{Al}_2\text{O}_3$. In particular, Ni/Ce06 and Ni/Ce10 produced amounts more than 20% greater than that obtained using $\text{Ni}/\text{Al}_2\text{O}_3$. These results indicate that CeO_2 is effective in promoting the activity of $\text{Ni}/\text{Al}_2\text{O}_3$ for hydrogen production, particularly when it is added to Al_2O_3 prior to Ni addition.

The average amounts of hydrogen obtained using Ni-CeX and Ni/CeX over a reaction period of 5 h increased with an increase in the CeO_2 loading up to ca. 5 wt%, as shown in Fig. 4. The maximum activities of Ni-CeX and Ni/CeX were achieved at CeO_2 contents of

Table 1. Textual properties of sample catalysts

Catalyst	S_{BET}^a (m^2/g) [(relative value)]	Average pore diameter ^a (nm)	Ni dispersion ^b (%) [(relative value)]
$\gamma\text{-Al}_2\text{O}_3$	206.6 (1.00)	9.2	
$\text{Ni}/\text{Al}_2\text{O}_3$	195.0 (0.94)	9.3	5.5 (1.00)
Ni-Ce02	186.2 (0.90)	9.0	
Ni-Ce04	180.9 (0.88)	9.2	2.3 (0.42)
Ni-Ce06	175.4 (0.85)	9.3	
Ni-Ce10	173.8 (0.84)	9.0	
Ni-Ce20	159.7 (0.77)	8.2	
Ni/Ce02	183.3 (0.89)	9.0	
Ni/Ce04	180.5 (0.87)	9.1	
Ni/Ce06	176.8 (0.86)	9.0	7.1 (1.29)
Ni/Ce10	167.1 (0.81)	9.0	
Ni/Ce20	152.8 (0.74)	8.5	

^aMeasured by N_2 physisorption

^bMeasured by H_2 chemisorption

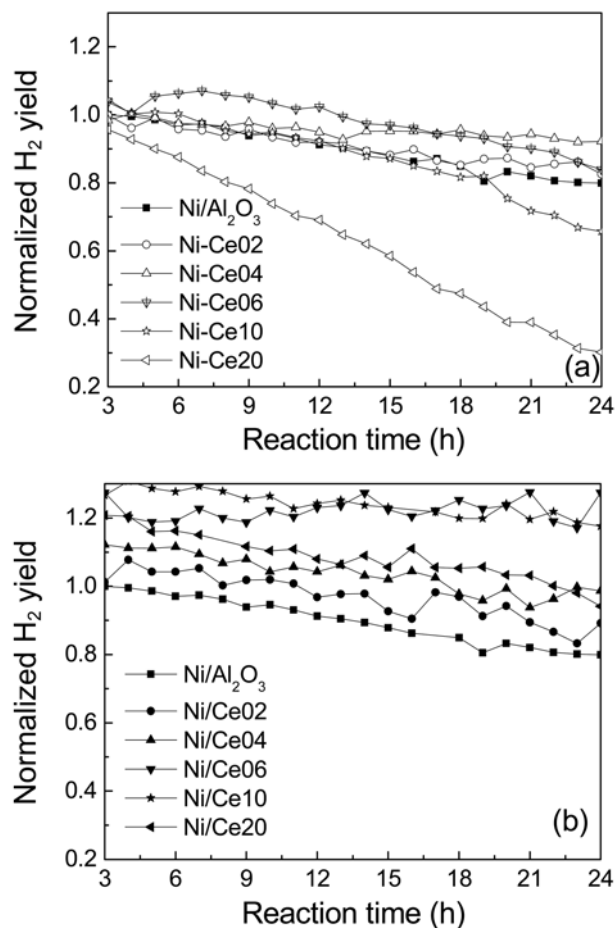


Fig. 3. H₂ yield, normalized to the initial H₂ yield of Ni/Al₂O₃ at 3 h, obtained using (a) Ni-CeX and (b) Ni/CeX: H₂O/C/O=3/3/0.25, reaction temperature=600 °C, total flow=68.8 ml/min.

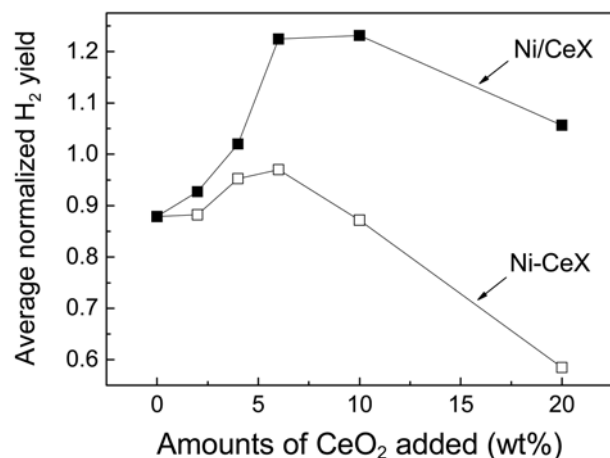


Fig. 4. Average H₂ yield obtained using Ni-CeX and Ni/CeX as a function of CeO₂ loading: H₂O/C/O=3/3/0.25, reaction temperature=600 °C, total flow=68.8 ml/min.

4 and 6 wt%, respectively, and then the activity decreased at higher CeO₂ loadings regardless of the CeO₂-impregnation sequence. Apparently the activity decreased because excess amounts of added CeO₂

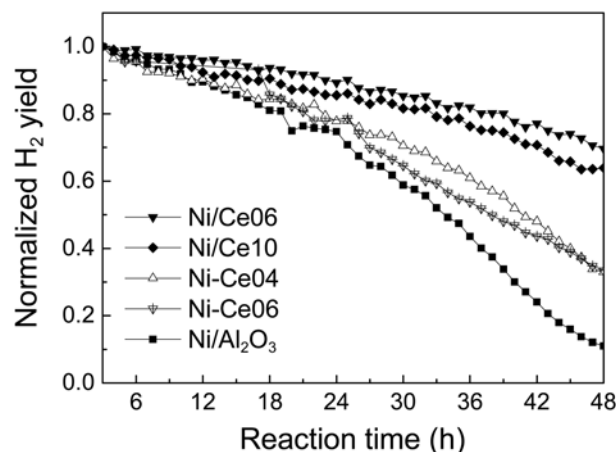


Fig. 5. Changes in the H₂ yield obtained using sample catalysts as a function of reaction time: H₂O/C/O=3/3/0.25, reaction temperature=600 °C, total flow=68.8 ml/min.

blocked the pore mouth of the catalysts to decrease the BET surface area as shown in Table 1. Accordingly, Ni/Ce06 showed the highest activity among the prepared catalysts with the average amount of hydrogen being larger by a factor of 1.25 than that of Ni-Ce04.

3. Deactivation Behavior

Fig. 5 shows the deactivation behaviors of the catalysts, which are depicted by changes in the hydrogen yield normalized to the initial values of individual catalysts, as a function of reaction time. In the case of Ni/Al₂O₃, the hydrogen yield decreased by 25% of the initial value during an initial reaction period of 24 h, after which the yield rapidly decreased to 11% of the initial one. Ni-CeX showed the same trend as Ni/Al₂O₃, i.e., Ni-Ce04 and Ni-Ce06 were deactivated moderately during a period of 24 h and the hydrogen yield rapidly decreased to 33% of the initial value in 48 h. On the other hand, the deactivation behavior of Ni/CeX differs from that of Ni/Al₂O₃, i.e., Ni/Ce06 and Ni/Ce10 maintained 70% and 64% of the initial hydrogen yields even after a reaction period of 48 h. These results indicate that CeO₂, when added to Al₂O₃ prior to Ni, drastically suppresses the deactivation of the catalysts by retarding the coke formation.

Fig. 6 shows changes in the mole fractions of products obtained with Ni/Al₂O₃, Ni-Ce04 and Ni/Ce06 as a function of reaction time. The initial product distribution (H₂; 54-57%, CO₂; 24-28%, CH₄; 10-11%, CO; 7-8%), which was nearly the same for the three catalysts, deviated from the thermodynamic equilibrium (H₂; 62.3%, CO₂; 11.8%, CH₄; 14.7%, CO; 11.2%), indicating that individual reactions did not reach equilibria under the reaction condition of this study. As the catalysts were deactivated with reaction time, the mole fractions of H₂ and CO₂ decreased and those of CO and CH₄ increased because the equilibrium of water-gas shift reaction was shifted to the reverse pathway on deactivated catalysts [24]. In this study, these changes were observed with Ni/Al₂O₃ and Ni-Ce04 after reaction for 24 and 36 h, respectively. However, in the case of Ni/Ce06, the initial mole fractions of the products were maintained up to a reaction period of 48 h.

4. Coke Analysis

Table 3 lists the amounts of coke deposited on the catalysts after use in the reaction for 48 h. The coke amounts decreased in the se-

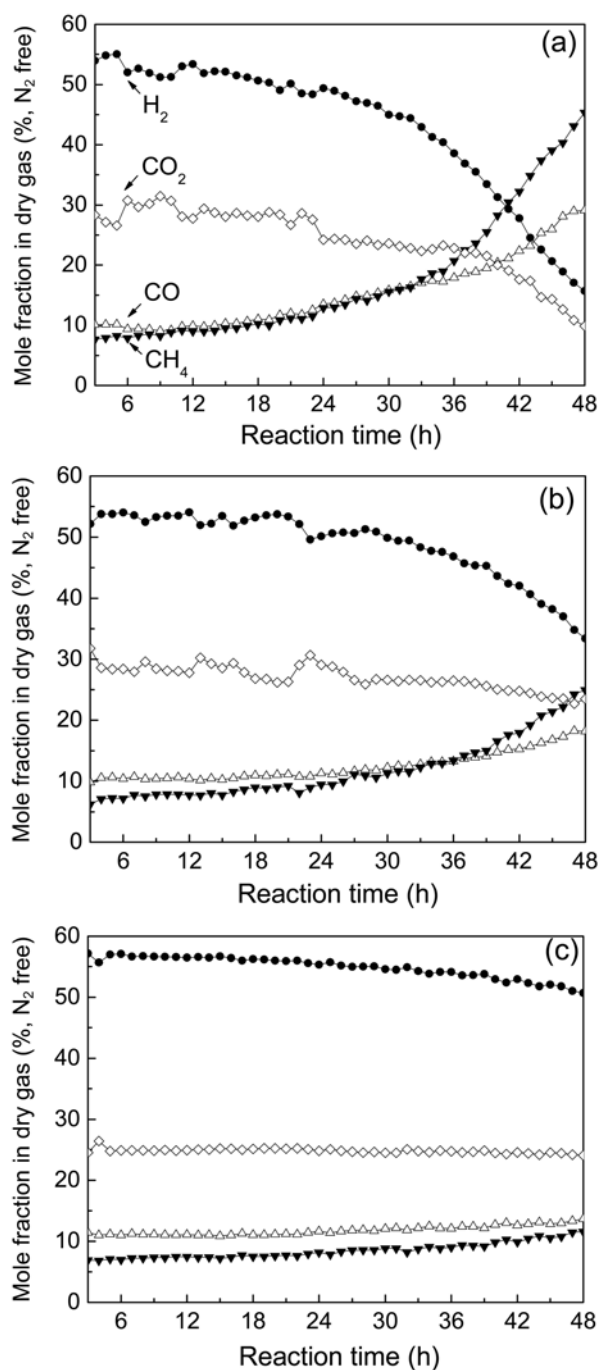


Fig. 6. Mole fraction of products as a function of reaction time for (a) Ni/Al₂O₃, (b) Ni-Ce04 and (c) Ni/Ce06: H₂O/C/O=3/3/0.25, reaction temperature=600 °C, total flow=68.8 ml/min.

quence of Ni/Al₂O₃>Ni-Ce04>Ni/Ce06. The TGA results obtained using the deactivated catalysts (Fig. 7(a)), which showed a significant weight loss between 350 °C and 700 °C due to the gasification of coke, also indicated a similar trend as observed with the EA results. The results of a differential thermogravimetric analysis (DTGA), Fig. 7(b), obtained from the TGA curves indicate peaks observed in three temperature region: peak I observed at temperatures below 500 °C only in the cases of CeO₂-added catalysts, peak II in the 500–600 °C region, and peak III observed at temperatures higher than

Table 3. EA result of deactivated catalysts obtained after reaction at 600 °C for 48 h

Catalyst	Weight percentage (wt%)		
	C	H	H/C
Ni/Al ₂ O ₃	46.4	0.6	0.15
Ni-Ce04	37.2	0.6	0.19
Ni/Ce06	34.8	0.6	0.21

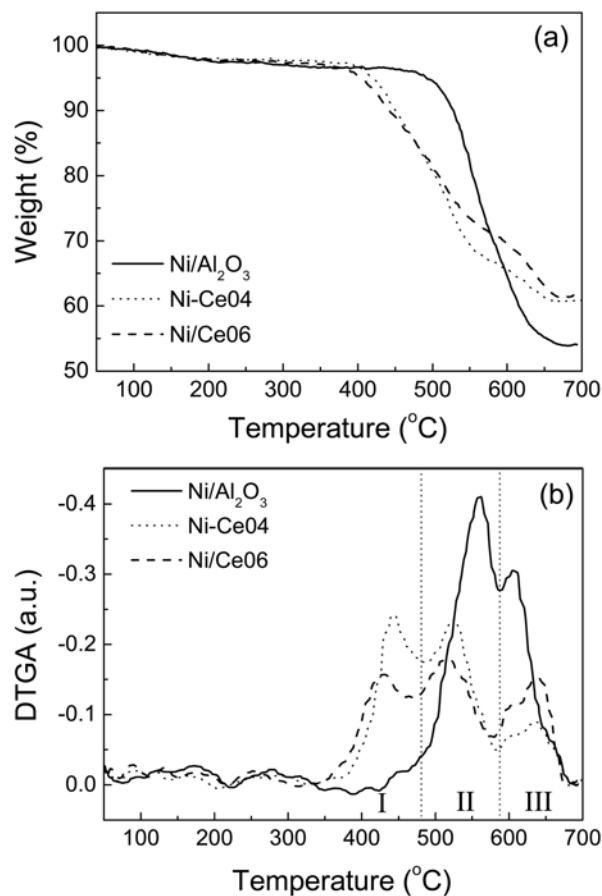


Fig. 7. Coke analysis for deactivated Ni/Al₂O₃, Ni-Ce04 and Ni/Ce06 (deactivated catalysts were obtained after reaction at 600 °C for 48 h): (a) TGA profile (10%O₂/N₂, flow rate=30 ml/min, ramping temperature=10 °C/min); (b) DTGA profile.

600 °C. It is apparent from the results that the coke species which are relatively reactive, or the reversible coke represented by peak I, are generated by the addition of CeO₂ to the catalysts. Furthermore, the coke species become more reactive, as indicated by the location of peak I, when CeO₂ is added prior to Ni addition (Ni/Ce06), instead of adding in the opposite order (Ni-Ce04). The amounts of the coke species represented by peaks II and III, which are less reactive than one represented by peak I and can be classified as refractory coke, are decreased in the CeO₂-added catalysts compared with the case of unpromoted Ni/Al₂O₃ catalyst. The amounts of the refractory coke were similar between the two CeO₂-added catalysts, Ni/Ce06 and Ni-Ce04.

DISCUSSION

This study has been focused on the effect of added CeO₂ and the sequence of CeO₂ addition on the performance of Ni catalysts in iso-octane ATR. In most studies about the CeO₂-containing catalysts for reforming processes, CeO₂ was used as a promoter or support [18-21]. However, as noted in Sections 3.2 and 3.3, added CeO₂ showed different effects on the activity of Ni/Al₂O₃ for iso-octane ATR depending on the impregnation sequence. That is, CeO₂ contained in Ni/CeX enhanced the hydrogen yield and retarded catalyst deactivation to a greater extent than one contained in Ni-CeX.

In the case of Ni-CeX, the Ni active sites on the surface are expected to be covered with subsequently added CeO₂ particles, leading to a decrease in the percentage of Ni exposed as demonstrated in Table 1. Nevertheless, the overall activity of Ni-CeX for ATR is slightly higher than that of Ni/Al₂O₃ because the added CeO₂ carries an intrinsic activity for the partial oxidation and steam reforming of iso-octane, and therefore is responsible for the production of additional amounts of hydrogen [25].

An increase in the activity of Ni/CeX can be explained by two reasons. First, there is an increased amount of NiO, a known active component for the reforming process, as confirmed by TPR results (Fig. 2 and Table 2). The added CeO₂, which interacts with the alumina support, suppresses the interaction between Ni and Al₂O₃ that leads to the formation of NiAl₂O₄ and promotes the formation of NiO on the support during the calcination step. The second reason is because the percentage of Ni exposed to the surface is increased, as shown in Table 1.

It is well known that the CeO₂ contributes to the suppression of coke formation, which is the main reason for catalyst deactivation in ATR, due to its oxygen storage capacity [20]. In the present study, the same effect of CeO₂ was also observed in the results of EA and TGA (Table 3 and Fig. 7). However, the total amounts of coke formed on Ni-CeX (37%) and Ni/CeX (35%), shown in Table 3, were not perfectly consistent with the deactivation rates of the catalysts (Fig. 5), which suggests that a specific type of coke was responsible for the catalyst deactivation.

According to Lee et al. [26], the deactivation of Ni catalysts was affected by the amounts of the refractory carbon species which were not readily gasified to CO and CO₂ in the CO₂ reforming of CH₄. It was also reported that the gasification temperature was lower for the refractory coke species that were present on the surface of Pt than for those formed on the surface of Al₂O₃ [27]. Therefore, the amounts of the refractory coke formed on the Ni were closely related to the catalyst deactivation. In this study, the area of peak II observed at temperatures ranging from 500 to 600 °C in DTGA (Fig. 7(b)), which represented the amount of the refractory carbon species on the Ni, showed the same trend as the deactivation rates of individual catalysts (Fig. 5). Accordingly, it can be proposed that even though the overall amount of coke on Ni/Ce06 is nearly the same as that on Ni-Ce04, the deactivation rate is lower for the former than for the latter because the amount of the refractory coke on the Ni is smaller for the former than for the latter.

CONCLUSIONS

CeO₂-added Ni catalysts exhibited improved hydrogen yield and

catalyst lifetime in the ATR of iso-octane compared with the case of unpromoted Ni/Al₂O₃. The performance of the CeO₂-promoted catalysts was also affected by the sequence of CeO₂ and Ni addition in the preparation step. Based on the results of reaction tests and catalyst characterization, the following conclusions are obtained.

1. Among the two kinds of CeO₂-modified Ni/Al₂O₃, Ni/CeX, which was prepared by CeO₂ impregnation followed by Ni impregnation, showed higher hydrogen yields and was deactivated more slowly compared with Ni-CeX, prepared by the opposite impregnation sequence, and Ni only catalyst. In particular, Ni/Ce06, which was prepared by adding 6 wt% of CeO₂ prior to the addition of Ni, showed the highest hydrogen yield and the slowest deactivation rates among the prepared catalysts.

2. CeO₂ in Ni/CeX enhanced the Ni dispersion and the formation of NiO by suppressing NiAl₂O₄ formation, unlike the case of Ni-CeX, because added CeO₂ interacted with Al₂O₃ to hamper the Ni-Al₂O₃ interaction.

3. Regardless of the impregnation sequence, added CeO₂ decreased coke formation due to its oxygen storage capacity under the severe condition of ATR, leading to the suppressed catalyst deactivation. In particular, Ni/Ce06 produced the least amount of the refractory coke species on the Ni among the catalysts of this study.

ACKNOWLEDGMENTS

This study was supported by GS Caltex Corp., Brain Korea 21 (BK21) project, National Research Laboratory (NRL) program and the Center for Ultramicrochemical Process systems (CUPS).

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