Synthesis Gas Production *via* Partial Oxidation, CO₂ Reforming, and Oxidative CO₂ Reforming of CH₄ over a Ni/Mg-Al Hydrotalcite-type Catalyst

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요 약

합성가스를 생산하기 위한 부분산화, 이산화탄소 리포밍, 메탄에 의한 산화CO₂ 리포밍 공정들은 니켈 하이드로탈사이트(Ni_{0.5}Mg_{2.5}Al) 촉매를 이용하여 수행되었고 안정한 이중층 구조를 형성시키기 위한 금속지지체(Mg, Ca)의 영향에 대해서도 다양한 연구가 진행되었다. 지지체전구물질(Mg, Ca)에 따라 메탄 리포밍의 안정성은 활성니켈이온과 지지체금속이온 사이의 결합강도차이에 의해 영향을 받는다. Ni-Mg-Al 구성체는 가장 안정한 하이드로탈사이트 이중층 구조이지만 Ni-Ca-Al 구성체는 그렇지 않다. 이산화탄소 리포밍 장기테스트에서 Ni-Mg-Al 촉매는 약 100시간 동안 80%의 효율을 유지하면서 탁월한 안정성을 보였지만 Ni-Ca-Al 촉매는 반응초기에 불활성화됨을 확인할 수 있었다. 활성금속 Ni과 지지체 Mg-Al 사이의 결합강도를 확인하기 위해 승온 환원(temperature-programmed reduction, TPR) 분석을 시행하였다. 이를 통해 Ni-Mg-Al 촉매가 Ni-Ca-Al 촉매보다 Ni의 환원온도가 더 높음을 확인할 수 있었다. Ni_{0.5}Ca_{2.5}Al 촉매는 가장 높은 초기반응성을 보였지만 코크형성으로 인해 반응성이 빠르게 감소하였다. 결론적으로 Ni_{0.5}Mg_{2.5}Al 촉매가 코크형성에 대한 강한 저항성을 갖고 있기 때문에 다른 촉매들보다 높은 반응성과 안정성을 갖는 것으로 보여진다.

주제어 : 메탄부분산화, 이산화탄소 리포밍, 산화개질, 하이드로탈사이트

Abstract : Partial oxidation, CO₂ reforming and the oxidative CO₂ reforming of CH₄ to produce synthesis gas over supported Ni hydrotalcite-type (Ni_{0.5}Mg_{2.5}Al catalyst) catalysts were carried out and the effects of metal supports (i.e., Mg and Ca) on the formation of a stable double-layer structure on the catalysts were evaluated. The CH₄ reforming stability was determined to be affected by the differences in the interaction strength between the active Ni ions and support metal ions. Only a Ni-Mg-Al composition produced a highly stable hydrotalcite-type double-layered structure; while the Ni-Ca-Al-type composition did not. Such structure provides excellent stability for the catalyst (~80% efficiency) as confirmed by the long-term CO₂ reforming test (~100 h), while the Ni-Ca-Al catalyst exhibited deactivation phases starting at the beginning of the reaction. The interaction strength between the active metal (Ni) and the supporting components (Mg and Al) was determined by temperature-programed reduction (TPR) analyses. The affinity was also confirmed by the TPR temperature because the Ni-Mg-Al catalyst required a higher temperature to reduce the Ni relative to the Ni-Ca-Al catalyst. The highest initial activity for synthesis gas production was observed for the Ni_{0.5}Ca_{2.5}Al catalyst; however, this activity decreased quickly due to coke formation. The Ni_{0.5}Mg_{2.5}Al catalyst exhibited a high reactivity and was more stable than the other catalysts because it had a higher resistance to coke formation.

Keywords : Methane partial oxidation, CO₂ reforming, Oxidative reforming, Hydrotalcite

1. Introduction

In recent years, the replacement of fossil fuels has received much attention as a result of various environmental issues as well as the limited amount of resources[1]. Therefore, the utili-

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zation of natural gas (mainly CH₄) for useful energy applications in transportation, such as methanol, hydrogen, or synthesis gas, is an attractive technology. There are many approaches to develop of highly resistant catalysts for the CH₄ reforming process and improve simultaneously the lifetime of the catalysts. One of the most common active metal components is Ni supported by stable materials (i.e.; Al₂O₃). Supported Ni catalysts are the typical choice for methane reforming, with Ni metal being an active component in CH₄ dissociation[2-4]. Typically, supported Ni catalysts are prepared by the wet-impregnation method. However, the catalysts prepared by wet-impregnation are often not fully capable of reduction by H₂ and the active Ni metal is often not homogeneously distributed on/in the catalyst [5]. Additionally, Ni particles typically sinter during reformation reactions at high temperatures[6], and the larger Ni particle sizes promote carbon formation. Under reforming conditions, catalyst deactivation also leads to a reduction in pressure due to the build-up of carbonaceous species[4,7,8]. A catalyst with a homogeneously distributed active sites would therefore be more resistant to sintering and coke formation under extreme conditions[9-12]. Hydrotalcite (HT)-like compounds, a class of layered double hydroxides (LDHs), contain 2+ and 3+ metal ions randomly distributed throughout the layered structure. The Mg-Al HT precursors, based on [Mg_{1-x}Al_x³⁺(OH)₂]^{x+}(CO₃²⁻)_x·mH₂O, in which a portion of the Mg²⁺ ions can be replaced by Ni²⁺, contain exchangeable anions located within the layered structure[6,9,13,14]. Upon high temperature calcination, this type of catalyst maintains a high surface area. Additionally, the HT-type compounds contain very small crystallites comprising oxide mixtures, which are stable during high temperature reactions and can also be reduced to thermally stable metal particles[15, 16]. These attributes render the Mg-Al HT, with Ni substitution, an optimal catalyst candidate for reforming reactions. In recent years, many investigations have been conducted to increase the stability of the HT-type catalysts by adding promoters. For example, Yu inserted La into the Ni-Mg-Al HT catalyst to inhibit carbon formation and enhance CO₂ adsorption.

Eq. (1) represents the general expression of the combined partial oxidation reaction where CO₂ reforming is converted to CH₄, where x represents the amount of CO₂ added. The stoichiometric amount of oxygen can then be determined by the amount of CO₂ present. If x is zero, then Eq. (1) is equivalent to the partial oxidation reaction, Eq. (2). If x is 6, then Eq. (1) is equivalent to the CO₂ reforming reaction, Eq. (3). Changing x between 0 and 6 changes the H₂/CO ratio between 2 and 1. Therefore, by varying x , the resulting synthesis gas ratio (i.e. H₂/CO ratio) can be tailored to be between 2 and 1. For methanol production, the conversion of CO₂ reforming of methane would require an additional process to adjust the H₂/CO ratio because

it results in a synthesis gas ratio less than 2[17,18]. The partial oxidation of CH₄, which meets the H₂/CO ratio of 2 for downstream methanol production, is difficult to control due to the formation of hot-spots and the subsequent risk of explosion[2]. In the oxidative CO₂ reforming of CH₄ (where x ranges from 0 to 6 in Eq. (1)), the H₂/CO ratio can be controlled by adjusting the feed ratio of O₂ and CO₂. Therefore, the oxidative CO₂ reforming of CH₄ is an interesting approach to synthesis gas production, especially for downstream applications with specific H₂/CO ratio needs, such as methanol synthesis or the Fischer-Tropsch process[19]. Additionally, the oxidative CO₂ reforming of CH₄ overcomes some of the limitations of independent partial oxidation and CO₂ reforming reactions[20]. For example, CO₂ reforming of CH₄ is endothermic and typically requires a substantial heat input to maintain the reaction temperatures. However, combining it with the partial oxidation reaction results in a lower energy input being required to maintain the catalyst bed at high temperatures, because the exothermic partial oxidation reaction can provide the heat for the endothermic reforming component[13].

As described above, a variety of catalysts have been previously employed in steam reforming, partial oxidation, and dry reforming to produce synthesis gas. However, most of these studies did not include long-term experiments to determine the stability of the HT-type catalyst. In this study, a typical Ni-Mg/Al HT-type catalyst was used for synthesis gas production. Additionally, the effects of various cations on the formation of the HT-type catalyst were evaluated with respect to stability.

2. Experimental

2.1. Catalyst preparation

Two co-precipitated catalysts (Ni_{0.5}Mg_{2.5}Al and Ni_{0.5}Ca_{2.5}Al) were prepared. The preparation procedure for both catalysts was identical, with either Mg or Ca nitrates being used as the precursors. For the preparation of the Ni_{0.5}Mg_{2.5}Al catalyst, 30 mL of a 1 M Ni nitrate (Ni(NO₃)₂·6H₂O, Puratronic[®], 99.9985%) aqueous solution, 150 mL of a 1 M Mg nitrate (magnesium nitrate hexahydrate, Alpha-Aesar, ACS grade 98.0-102.0%) aqueous solution and 60 mL of a 1 M Al nitrate (Al(NO₃)₃·9H₂O, Alpha-Aesar, ACS grade 98.0-102.0%) aqueous solution were prepared and mixed. The mixed nitrate solution was then

added drop-wise into 240 mL of a 0.50 M Na₂CO₃ aqueous solution at room temperature under vigorous stirring (400 rpm). A 3.0 M NaOH aqueous solution was simultaneously added drop-wise to maintain the pH at 10.0 ± 0.1. The resulting precipitate was aged in the mother liquor at 120 °C for 12 h. The aged precipitate was then cooled to room temperature and held for 1 h. The precipitate was then washed and filtered with distilled and de-ionized water until the residual Na⁺ in the aged precipitate was removed (pH -7). The washed precipitate was then dried at 120 °C for 12 h. The Ni_{0.5}Ca_{2.5}Al catalyst was prepared in the same manner using a mixture of 30 mL of 1 M Ni nitrate, 150 mL of 1 M Ca nitrate (Ca(NO₃)₂·4H₂O, Alpha-Aesar, ACS grade 98.0-102.0%), and 60 mL of 1 M Al nitrate. In preparing the 10 wt% Ni/Al₂O₃ catalyst, -75 mL of distilled water was heated to 80 °C while stirring, and γ-Al₂O₃ powder (Alpha-Aesar, 99.97% (metal basis)) was then added to the distilled water. 1 M Ni nitrate was added drop-wise, until the target 10 wt% of Ni relative to the Al₂O₃ was obtained. For all catalysts, water was evaporated under continuous stirring at 80 °C. The resulting residue was then heated in an oven at 120 °C for 12 h, and the dried precipitate was crushed to powder form. The powder precipitates were calcined at 850 °C in air for 5 h to produce an oxide-phase catalyst. The calcined catalysts were pelletized to attain a particle size of 354-500 μm.

2.2. Catalyst characterization

The catalyst crystal structures of the fresh and spent catalysts were characterized using X-ray diffraction (XRD). Powder XRD patterns were measured on a Rigaku D/Max-III C using standard Bragg-Brentano geometry with Ni-filtered Cu Kα radiation (λ₁ = 1.5406 Å, λ₂ = 1.5444 Å) and 40 kV/100 mA X-ray radiation. The XRD data were collected in the range of 5° to 80° 2θ range using a step size of 0.01 and a count time of 1 s. The diffraction patterns were identified upon comparison with spectra in the JCPDS data base (International Centre for Diffraction Data, USA). Catalyst surface areas were measured using a Micromeritics Gemini 3 2375. Approximately 100 mg of the pelletized catalysts (particle size in the range 354-500 μm) was loaded and the surface area was measured at -196 °C, using liquid nitrogen as the adsorbate. Eleven points within the P/P₀ range of 0.05 and 0.3 were collected and used to produce the BET plot and subsequently calculate the surface area. The BET surface areas of the Ni_{0.5}Mg_{2.5}Al, Ni_{0.5}Ca_{2.5}Al, and Ni/Al₂O₃ catalysts after calcination and reduction are listed in Table 1 and compared to some reference values. After reduction in 10% H₂/N₂ at 720 °C for 1 h, the surface areas increased, which implied re-construction of the catalyst surfaces. The Ni_{0.5}Ca_{2.5}Al catalyst had the highest increase in surface area after reduction.

The catalyst morphology was examined using scanning elec-

Table 1. Catalyst surface areas after calcination and reduction

Catalysts	After calcination ^{a)} (m ² /g)	After reduction ^{b)} (m ² /g)	References
10 wt% Ni/Al ₂ O ₃	191.0	191.2	This work
Ni _{0.5} Ca _{2.5} Al	33.2	55.7	
Ni _{0.5} Mg _{2.5} Al	149.0	153.0	
spc-Ni/Mg-Al	-	161.0	[18]
spc-Ni/Ca-Al	-	14.6	
imp-Ni/Al ₂ O ₃	-	95.0	
Ni _{0.5} /Mg _{2.5} (Al)O	158.0	-	[17]
13.5 wt% Ni/γ-Al ₂ O ₃	106.3	-	

^{a)} Calcined at 1,123 K for 5 h in air

^{b)} Reduced at 993 K for 1 h in 10% H₂/N₂

tron microscopy (SEM). A Leo FESEM 1530 SEM was utilized in this investigation, and the vacuum pressure was less than 1.5 × 10⁻⁵ mbar. TPR and TPO were also used to characterize the catalysts. For the TPR test, 100 mg of the calcined catalyst was placed in a quartz tube and the temperature was ramped at 10 °C/min from 25 to 800 °C in the presence of a 10% H₂/N₂ reducing gas mixture flowing at 30 mL/min. A thermal conductivity detector (TCD) was then used to measure the amount of H₂ consumption. The amount of coke produced during the CO₂ reforming of CH₄ was determined by TPO in a Hiden Catlab micro-reactor system. 25 mg of the spent catalyst was placed in the quartz tube and a 30 mL/min 10% O₂/He gas mixture was utilized. The sample temperature was increased from 25 °C to 850 at 10 °C/min.

2.3. Catalytic reaction tests

A fixed-bed reactor was designed to examine the catalyst performances. The catalyst bed resided in a 10 mm I.D. quartz tube with a highly porous quartz frit to support the catalyst. A thermocouple located at the top of the catalyst bed was used to control the furnace temperature. Before the reaction tests, the effects of the external and internal mass transfer limitation at a constant GHSV of 240,000 cm³/g-h were examined. For the external mass transfer, a fixed residence time (W/F = 0.015) through a variety of feed velocities (50, 100, 150, 200 and 250 mL/min of total feed) at 700 °C was chosen. The internal mass transfer was evaluated using a feed mixture composed of CH₄/CO₂/N₂ = 1/1/3 at 700 °C for various sizes of catalysts (average 303, 427, and 605 μm). When the CH₄ consumption rate was unchanged for the external and internal mass transfer limitations, the reaction can then be controlled by the reaction limitation instead of the diffusion limitation. The activation energy of CH₄ and CO₂ consumption was determined by the Arrhenius

plot. For each reaction test, 50 mg of the calcined catalyst with a particle size between 354-500 μm was diluted with 400 mg of SiC (422-599 μm). The SiC was used to prevent an increase in pressure due to coke formation and subsequently improve the thermal dispersion throughout the catalyst bed. The catalysts were reduced *in situ* at 720 $^{\circ}\text{C}$ in 200 mL/min of 10% H_2/N_2 for 1 h. After the reduction, the bed temperature was reduced to the desired reaction temperature under 100% N_2 . During the catalyst activity tests, the total gas flow rate was set to 200 mL/min (80 mL/min of reactant gases and 120 mL/min of N_2). The feed ratio for the partial oxidation of CH_4 was $\text{CH}_4/\text{O}_2/\text{N}_2 = 26/14/60$ and for CO_2 reforming of CH_4 was $\text{CH}_4/\text{CO}_2/\text{N}_2 = 20/20/60$. For the oxidative CO_2 reforming of CH_4 , the x represented the amount of CO_2 added in Eq. (1) was (4) in this study. The ratio was therefore $\text{CH}_4/\text{CO}_2/\text{O}_2/\text{N}_2 = 21.8/14.5/3.6/60$, and the stoichiometry corresponding to $x = 4$ is shown in Eq. (4).

The resulting gases were collected and sampled using a gas chromatography (GC) column (Varian CP-3800 with a Carboxen-1000) to quantify the components of the product gases. The CH_4 conversion rate (Eq. (5)) and the synthesis gas ratio, H_2/CO , (Eq. (6)) were calculated from the concentrations measured by GC, which were then converted into molar flow rates. The activation energy of CH_4 and CO_2 were calculated from the Arrhenius plot (Eq. (7)).

$$-r'_{\text{CH}_4} \left(\frac{\text{mol}}{\text{g}_{\text{cat}} \cdot \text{sec}} \right) = \frac{dF_{\text{CH}_4}}{dW} = \frac{X_i \times F_i (\text{mol/min})}{W_{\text{cat}} (\text{g})} \quad (5)$$

$$\text{H}_2/\text{CO ratio} = \frac{n_{\text{H}_2, \text{out}}}{n_{\text{CO}, \text{out}}} \quad (6)$$

For the pre-treatment, the catalysts were reduced at 720 $^{\circ}\text{C}$ in 10% H_2/N_2 for 1 h. The three reactions-partial oxidation, CO_2 reforming, and oxidative CO_2 reforming of CH_4 -were carried out with a GHSV = 240,000 $\text{cm}^3/\text{g}\cdot\text{h}$ at 700 $^{\circ}\text{C}$ for 20 h during the first set of experiments.

3. Results and discussions

3.1. Catalyst activities

3.1.1. External and internal mass transfer limitation

Reliable kinetic data could be obtained when the mass transfer limitation (external and internal) was negligible. The effects of the feed flow rate and catalyst particle size on the reaction rate were experimentally determined using a feed mixture composed of $\text{CH}_4/\text{CO}_2/\text{N}_2$ (1/1/3) at 700 $^{\circ}\text{C}$. For the external diffusion, a

constant rate ($W/F = 0.015 \text{ g}\cdot\text{s}/\text{mL}$) was applied in order to maintain the amount of contact time. The effects of the flow rate with a consistent amount of contact time are shown in Figure 1. It is clear that the rate of CH_4 consumption increased until the flow rate was 200 mL/min. This result indicated that up to the flow rate of 200 mL/min, the external mass transfer had some influence on the overall reaction rate. However, when the flow rate exceeded 200 mL/min, the rate of CH_4 consumption remained constant. Therefore, experiments with a flow rate of 200 mL/min are adequate to obtain reaction data that are not masked by the external transport limitation.

In order to investigate the possible effects of internal diffusion limitation, three different particle sizes were tested: (i) 251-354 μm (average 303 μm), (ii) 354-500 μm (average 427 μm), and (iii) 500-710 μm (average 605 μm). The flow rate was chosen to be 200 mL/min based on the external limitation. The

Figure 1. External mass transfer limitation (Catalyst: $\text{Ni}_{0.5}\text{Mg}_{2.5}\text{Al-HT}$; $W/F = 0.015$ at 700 $^{\circ}\text{C}$).

Figure 2. Internal mass transfer limitation (Catalyst: $\text{Ni}_{0.5}\text{Mg}_{2.5}\text{Al-HT}$; Feed flow rate = 200 mL/min at 700 $^{\circ}\text{C}$).

effects of the particle size on the rate of CH₄ consumption is shown in Figure 2. It was clear that the rate of CH₄ consumption was independent of the average diameter of the particles. This result indicated that particle sizes between 250 and 700 μm are small enough for the reaction to not be affected by internal mass limitation at 700 $^{\circ}\text{C}$.

3.1.2. Partial oxidation of CH₄

The conversions attained during the CH₄ partial oxidation and the resulting synthesis gas ratios (H₂/CO) are shown in Figure 3. All catalysts exhibited ~85% CH₄ conversion and the Mg- and Ca-containing samples exhibited no significant deactivation over the 20 h test. Additionally, the levels of reactivity were all determined to be near the equilibrium levels. The Ni/Al₂O₃ catalyst exhibited some deactivation beginning after 13 h of reaction, which confirmed that the Ni/Al₂O₃ catalyst deactivates over time, as confirmed by many other previous studies[21-23]. The synthesis gas ratios (H₂/CO ratio) obtained with each catalyst exhibited similar patterns. The Ni_{0.5}Mg_{2.5}Al and Ni_{0.5}Ca_{2.5}Al catalysts resulted in a syngas ratio of around 2, close to the theoretical level. This result indicated that since H₂ and CO were produced in proportion, the stoichiometry in Eq. (4) was applied and neither product was preferentially consumed via side reactions afterwards. The syngas ratio decreased with time over the Ni/Al₂O₃ catalyst, which corresponded to the reduced conversion. In conclusion, for the partial oxidation of CH₄, the two co-precipitated catalysts (Ni_{0.5}Mg_{2.5}Al and Ni_{0.5}Ca_{2.5}Al) exhibited stable reactivity for 20 h of reaction with conversions close to the equilibrium level and syngas ratios near the predicted values based on the reaction stoichiometry.

Figure 3. CH₄ conversion profiles and gas ratios (H₂/CO) for the CH₄ partial oxidation as a function of time for the three catalysts. Equilibrium values, calculated using ASPEN PlusTM, are also plotted (total gas flow rate: 200 mL/min; CH₄/O₂/N₂ = 26/14/60 vol%; GHSV = 240,000 cm³/g_{cat}-h).

3.1.3. CO₂ reforming of CH₄

Coke covering the active Ni sites will ultimately lower the activity of the catalyst. It is therefore assumed that the dry reforming is a good indicator of the carbon deposition resistance of a given catalyst. Under CO₂ reforming of CH₄, two reactions typically occur CO₂ reforming of CH₄ (Eq. (3)) and the reversible water-gas shift (RWGS) reaction (Eq. (8)). Therefore, in addition to the main reaction, the RWGS also affects the overall pathway. For example, due to the RWGS reaction, the syngas ratio (H₂/CO) for CO₂ reforming of CH₄ was always less than 1.

The CH₄ conversions at 700 $^{\circ}\text{C}$ for the three catalysts, along with the equilibrium conversion, are shown in Figure 4. At 700 $^{\circ}\text{C}$, the theoretical CH₄ conversion level was ~82%. The CH₄ conversion using the Ni_{0.5}Ca_{2.5}Al catalyst increased slightly at the beginning and reached the equilibrium CH₄ conversion (82%) within 4 h time-on-stream. However, after 4 h it slowly deactivated over time, decreasing from 82% to 75% after 20 h. This reduction was likely caused by carbon build-up on the surface, which was confirmed by TPO and will be discussed later. The Ni/Al₂O₃ catalyst exhibited continuous deactivation from an initial CH₄ conversion of 60%, decreasing to 48% conversion after 20 h. It is important to note that Ni/Al₂O₃ also had the lowest initial CH₄ conversion. Alternatively, the Ni_{0.5}Mg_{2.5}Al catalyst exhibited very stable conversion (~68%) compared to the other catalysts. This result indicates that the Ni_{0.5}Mg_{2.5}Al catalyst exhibited the highest resistance to deactivation. However, the conversion was lower than the equilibrium conversion, and lower than the conver-

Figure 4. CH₄ conversion profiles and synthesis gas ratios (H₂/CO) as a function of time for CO₂ reforming of CH₄ using the three different catalysts (total gas flow rate: 200 mL/min; CH₄/CO₂/N₂ = 20/20/60 vol%; GHSV = 240,000 cm³/g_{cat}-h).

sion obtained with the Ca-containing catalyst. The syngas ratios (H_2/CO ratios) were also less than unity due to the reverse water-gas shift (RWGS) reaction (Eq. (8)). Additionally, even though the CH_4 conversion over the three catalysts was distinguishable, the syngas ratios were very similar and all catalysts started with a ratio of -0.9, which was close to the equilibrium value. These results confirmed that the CH_4 conversions were dependent on the catalysts, but the synthesis gas ratios were not, which suggested that the same reaction pathway was occurring over each catalyst. These results also indicated that the RWGS reaction rapidly reaches equilibrium for CO_2 reforming of CH_4 at 700 °C.

During 20 h of time-on-stream, the $Ni_{0.5}Mg_{2.5}Al$ catalyst exhibited high stability, and the $Ni_{0.5}Ca_{2.5}Al$ catalyst exhibited deactivation. However, even after 20 h, the activity of the Ca-based catalyst was still higher than the Mg-based catalyst. It is therefore difficult to conclude after 20 h time-on-stream which of these two catalysts was better. Therefore, more prolonged experiments were performed at 100 h time-on-stream for these two catalysts. The pre-treatment processes were identical to those described previously. The experimental results for the $Ni_{0.5}Mg_{2.5}Al$ catalyst and the $Ni_{0.5}Ca_{2.5}Al$ catalyst are shown in Figure 5 for over 100 h of the dry reforming. The $Ni_{0.5}Mg_{2.5}Al$ catalyst exhibited a relatively stable reactivity based on the CH_4 conversion and the H_2/CO ratio. The CH_4 conversion decreased by about 4% over 100 h, from 67 to 63%. However, for the $Ni_{0.5}Ca_{2.5}Al$ catalyst, the deactivation trend observed during the first 20 h continued throughout 100 h. The CH_4 conversion decreased from 78 to 62% but the syngas ratio only slightly decreased. Based on these longer-term experiments, it was clear that the $Ni_{0.5}Mg_{2.5}Al$ catalyst suffered considerably less deactivation than the $Ni_{0.5}Ca_{2.5}Al$ catalyst and exhibited a much higher resistance

Figure 5. Long-term $Ni_{0.5}Mg_{2.5}Al$ and $Ni_{0.5}Ca_{2.5}Al$ catalytic performance profiles for CO_2 reforming of CH_4 (total gas flow rate: 200 mL/min; $CH_4/CO_2/N_2 = 20/20/60$ vol%; GHSV = 240,000 $cm^3/g_{cat}\cdot h$).

to coke formation, as will be discussed below. In conclusion, the $Ni_{0.5}Mg_{2.5}Al$ catalyst exhibited the highest stability, even though the activity remained lower than the equilibrium-based expectation. The $Ni_{0.5}Ca_{2.5}Al$ catalyst initially exhibited the highest activity, reaching equilibrium after about 4 h time-on-stream, but past 4 h its activity continuously decreased at a rate of -0.2%/h. Finally, the Ni/Al_2O_3 catalyst exhibited the worst reactivity and stability for the dry reforming.

3.1.4. Oxidative CO_2 reforming of CH_4

The basic concept of the oxidative CO_2 reforming of CH_4 is to combine the exothermic partial oxidation with the endothermic CO_2 reforming. The change in reaction enthalpy (ΔH) at 700 °C for the range of x [Eq. (1)] between 0 and 6 was simulated using ASPEN PlusTM, the results of which are shown in Figure 6. When x was 0, Eq. (1) represented the partial oxidation of the CH_4 reaction and when x was 6, it represented the CO_2 reforming of CH_4 . Figure 6 confirms that oxidative CO_2 reforming of CH_4 at 700 °C was an endothermic reaction when x was greater than 1. In order to confirm the ASPEN simulation (Figure 6) with actual experimental data, temperature data obtained during the experiments are shown in Figure 7. With the two reforming reactions, there was an immediate decrease in temperature, which then increased as the heat of the furnace compensated for the drop in temperature. For the partial oxidation reaction, the opposite process occurred. The oxidative reforming led to a smaller decrease in temperature relative to the dry reforming alone, confirming that the former requires less heat to maintain the reaction temperature while reducing the chance of hot spots formation as a result of partial oxidation.

Figure 6. Change in enthalpy (ΔH) at 700 °C as a function of the x value described in Eq. (1) (calculated using ASPEN PlusTM).

Figure 7. Temperature profiles during partial oxidation, CO₂ reforming, and the oxidative CO₂ reforming of CH₄ upon reducing the reaction temperature from 720 °C to 700 °C.

Figure 8. CH₄ conversion profiles and synthesis gas ratios (H₂/CO) for the oxidative CO₂ reforming of CH₄ on the three catalysts (total gas flow rate: 200 mL/min; CH₄/CO₂/O₂/N₂ = 21.8/14.5/3.6/60 vol%; GHSV = 240,000 cm³/g_{cat}-h).

The catalytic activities for the oxidative CO₂ reforming of CH₄ over the three catalysts are shown in Figure 8. Co-feeding O₂ with CH₄ and CO₂ was expected to reduce carbon deposition as a result of the increased oxidation of surface carbon species and also increase the conversion of CH₄ at high temperatures (~700 °C). The reactivities of the Ni_{0.5}Ca_{2.5}Al and Ni_{0.5}Mg_{2.5}Al catalysts during the initial period (< 5 h) were similar (~75%). The reactivity of the Ni_{0.5}Ca_{2.5}Al catalyst for oxidative CO₂ reforming of CH₄ was less than that of CO₂ reforming of CH₄;

however, the reactivity of the Ni_{0.5}Mg_{2.5}Al catalyst was quite similar. Since the feed for the oxidative CO₂ reforming of CH₄ contains oxygen that might oxidize surface carbon, the Ni_{0.5}Ca_{2.5}Al catalyst did not exhibit deactivation, and conversion actually slightly increased after 20 h of reaction. The syngas ratios for the catalysts were similar, even though the syngas ratio for the Ni/Al₂O₃ was slightly lower than that of the other catalysts. These trends (different conversions but same syngas ratios) were also observed in the partial oxidation and CO₂ reforming reactions, which suggested that the same reaction mechanisms existed over the three sample types. Additionally, except for the Ni/Al₂O₃ catalyst, the H₂/CO ratio was very close to its equilibrium value, which implied that the RWGS reaction reached equilibrium in the presence of the Ni_{0.5}Mg_{2.5}Al and Ni_{0.5}Ca_{2.5}Al catalysts at 700 °C.

Overall, based on the reactivity tests for all three sets of reactions, the Ni_{0.5}Mg_{2.5}Al catalyst exhibited the most stable reactivity among other catalysts under the most severe conditions (e.g. CO₂ reforming of CH₄). Additionally, the reactivity of the Ni_{0.5}Mg_{2.5}Al catalyst, although lower than the equilibrium conversion, still resulted in greater than 70% CH₄ conversion. The Ni_{0.5}Ca_{2.5}Al catalyst exhibited the highest initial CH₄ conversion for all reactions; however, its reactivity began to degrade shortly after the onset of the dry reforming test. Finally, as expected, the tests on oxidative CO₂ reforming of CH₄ exhibited conversions between those of the partial oxidation and the dry reforming. An important difference between the oxidative CO₂ reforming and dry reforming in the presence of the Ni_{0.5}Ca_{2.5}Al catalyst was that the reactivity was more active when oxygen was added and its activity decreased initially but eventually stabilized at a level similar to that of Ni_{0.5}Mg_{2.5}Al. Nonetheless, the Ni_{0.5}Mg_{2.5}Al catalyst exhibited superior stability under dry reforming and oxidative reforming.

3.1.5. Activation Energy and Effects of the Partial Pressures of CH₄, CO₂, and H₂

Typically, the kinetic studies were conducted at the temperature in which the conversion was far from the equilibrium. It was confirmed that the CH₄ consumption rate from the reactivity test (Figure 4) at 700 °C was lower than the equilibrium level. The temperature sensitivity of the CH₄ consumption rate for CO₂ reforming of CH₄ over the Ni_{0.5}Mg_{2.5}Al-HT catalyst was determined by the Arrhenius plot (Figure 9) in the temperature range of 650–750 °C at a constant GHSV of 240,000 cm³/g-h. It was clear that the support of Ni crystallites significantly influenced the activation energy by affecting the rate-controlling step in the reaction sequence. The activation energy for the consumption of CH₄ and CO₂ and the formation of H₂ and CO on the Ni_{0.5}Mg_{2.5}Al-HT catalyst were calculated to be 18.9, 18.0,

Figure 9. Arrhenius plot for CH₄ and CO₂ consumption at GHSV = 240,000 cm³/g*h; Feed composition: CH₄/CO₂/N₂ = 1/1/3 vol%).

25.3, and 18.7 kJ/mol, respectively. Based on the present investigation, it was determined that the rate determining step of CO formation closely corresponds to the CH₄ and CO₂ consumption step. One possible reason for obtaining a high energy barrier for H₂ formation was the RWGS process. Since the activation energy barrier of the CH₄ consumption step was slightly greater than that of the CO₂ consumption step, it was assumed that the CH₄ dissociation step could be the rate determining step. The lower activation energy barrier for CO₂ consumption might be caused by the presence of the strong Lewis base MgO, which can facilitate the activation of CO₂.

The influence of the partial pressures of CH₄, CO₂, and H₂ on the Ni_{0.5}Mg_{2.5}Al-HT catalyst at atmospheric pressure for the CH₄ consumption rate ($-r_{CH_4}$) was evaluated in the temperature range of 650–750 °C. A constant CO₂ (or CH₄) partial pressure of 20.26 kPa was used as the CH₄ (or CO₂) partial pressure was varied. N₂ gas was used to balance the total GHSV to 240,000 cm³/g-h for all conditions. As shown in Figure 10, the CH₄ consumption rate was strongly affected by the partial pressure of CH₄ at a CO₂ partial pressure of 20.26 kPa, since the CH₄ consumption rate increased as the CH₄ partial pressure increased. As shown in Figure 11, the CH₄ consumption rate was strongly influenced when the partial pressure of CO₂ was lower (in the range of 10.13 to 20.26 kPa) than the stoichiometric ratio. The CH₄ consumption rate was then unchanged at higher CO₂ partial pressures (>20.26 kPa). Therefore, it can be concluded that the reaction rate was more sensitive to the CO₂ partial pressure than to the CH₄ partial pressure when compared in the low partial pressure ranges (10.13 to 20.267 kPa). However, at high CO₂ and CH₄ partial pressures (>20.26 kPa), the CH₄ partial pressure exhibited a stronger influence on the CH₄ consumption rates than

Figure 10. CH₄ consumption rate as a function of P_{CH₄} at a constant P_{CO₂} of 20.26 kPa.

Figure 11. CH₄ consumption rate as a function of P_{CO₂} at a constant P_{CH₄} of 20.26 kPa.

Figure 12. CH₄ consumption rate as a function of P_{H₂} at a constant P_{CH₄} and P_{CO₂} of 20.26 kPa.

the CO₂ partial pressure. These results can be attributed to the stronger adsorption of CH₄ to the surface of the catalyst compared to that of CO₂ at higher partial pressures. Figure 12 displays the rates of CH₄ consumption at various partial pressures of H₂ at constant CH₄ and CO₂ partial pressures of 10.13 kPa. As the H₂ partial pressure increased, the rate of CH₄ consumption decreased because the reverse reaction and RWGS reaction then become dominant.

3.2. Catalyst characterization

3.2.1. Structure of fresh and spent catalysts

The fresh Ni_{0.5}Mg_{2.5}Al and Ni_{0.5}Ca_{2.5}Al catalyst crystal structures were investigated using XRD, and all diffraction patterns were matched with JPCDS references. The XRD patterns obtained from the Ni_{0.5}Mg_{2.5}Al sample (Figure 13) confirmed that the as-prepared samples contained a well-crystallized HT-type (or LDH) phase. The LDH structure for the Ni_{0.5}Mg_{2.5}Al catalyst implied that Ni²⁺ was incorporated in the Mg²⁺ site positions and dispersed uniformly throughout the brucite layer of the HT structure. In particular, a set of three reflection peaks at 2 θ values of 11.3, 22.7, and 34.5° indicated that the HT-type structure possessed a layered structure in which both Ni²⁺ and Al³⁺ substituted Mg²⁺ sites in the brucite-like sheet[15,24]. After calcination at 820 °C in air for 5 h, the HT peaks disappeared and MgO (at 37.0, 43.1, 62.6, and 79.0°) and NiO (at 37.0, 43.1, 62.6, 74.9, and 79.0°) peaks appeared and overlapped. After reduction at 720 °C in 10% H₂/N₂ for 1 h, the NiO peaks were weak and the Ni metal peaks at 44.1, 51.7, and 76.1° were clearly visible. This result indicated that during reduction, some of the NiO crystals transformed into active Ni metal phases, as expected. Therefore, the Ni_{0.5}Mg_{2.5}Al catalyst prepared by the

Figure 13. XRD patterns obtained from the Ni_{0.5}Mg_{2.5}Al catalyst: (a) fresh; (b) calcined at 820 °C in air for 5 h; (c) reduced at 720 °C in 10% H₂/N₂ for 1 h.

co-precipitation method clearly contained active Ni phases substituted into a portion of the Mg²⁺ phases, resulting in the Ni/Mg-Al HT-type catalyst[25]. After thermal treatment at 850 °C in air for 5 h, and the reduction by 10% diluted H₂/N₂ at 720 °C for 1 h, the active Ni phases within the LDH become the active catalytic metal.

For the Ni_{0.5}Ca_{2.5}Al catalyst, the XRD patterns of the fresh, calcined, and reduced catalysts are shown in Figure 14. The fresh Ni_{0.5}Ca_{2.5}Al catalyst did not exhibit the HT-like structure. However, after being calcined at 820 °C in air for 5 h, NiO, CaO, and Ca₁₂Al₁₄O₃₃ peaks appeared. Interestingly, Ni metal peaks were observed with the calcined Ni_{0.5}Ca_{2.5}Al catalyst but not with the Ni_{0.5}Mg_{2.5}Al catalyst, which implied that the Ni-Ca interaction was weaker than Ni-Mg interaction.

Figure 14. XRD patterns obtained from the Ni_{0.5}Ca_{2.5}Al catalyst: (a) fresh; (b) calcined at 820 °C in air for 5 h; (c) reduced at 720 °C in 10% H₂/N₂ for 1 h.

Figure 15. XRD patterns obtained from the Ni_{0.5}Mg_{2.5}Al catalyst (a) after reduction; (b) after partial oxidation of CH₄; (c) after CO₂ reforming of CH₄; (d) after the oxidative CO₂ reforming of CH₄.

Figure 16. XRD patterns after CO₂ reforming of CH₄ at 700 °C for 20 h from: (a) Ni_{0.5}Mg_{2.5}Al; (b) Ni_{0.5}Ca_{2.5}Al; (c) Ni/Al₂O₃ catalysts.

The XRD patterns of the spent Ni_{0.5}Mg_{2.6}Al catalysts after 20 h of partial oxidation, CO₂ reforming and the oxidative CO₂ reforming of CH₄ at 700 °C are shown in Figure 15. Both Ni metal and NiO phases were observed after CH₄ partial oxidation and the oxidative CO₂ reforming of CH₄. The oxygen species supplied for the partial oxidation of CH₄ and the oxidative CO₂ reforming of CH₄ likely oxidized some of the Ni. However, the H₂ or CO generated from the reactions can simultaneously reduce the formed NiO, subsequently regenerating the active Ni phases for further reactions, resulting in evidence of both chemical states being present. Additionally, a weak graphite peak was observed at 26.4° after CO₂ reforming of CH₄ and the oxidative CO₂ reforming of CH₄ tests, but not after the CH₄ partial oxidation. The likely reason for its absence during partial oxidation is that the C:O ratio was the lowest (26:28) compared to the other two processes.

The XRD patterns of the different catalysts after 20 h of CO₂ reforming of CH₄ at 700 °C are shown in Figure 16. The diffraction patterns of Ni_{0.5}Mg_{2.5}Al indicated the presence of both metal and oxide Ni, as well as MgO. However, the XRD data obtained from the Ni_{0.5}Ca_{2.5}Al exhibited weaker Ni peaks, with significantly less Ni metal being observed. Most importantly, much stronger graphite peaks were observed on the Ni_{0.5}Ca_{2.5}Al and Ni/Al₂O₃ catalysts than on the Ni_{0.5}Mg_{2.5}Al catalyst. These results implied that the Ni_{0.5}Mg_{2.5}Al catalyst had a stronger resistance to coke formation.

3.2.2. TPR of catalysts

The H₂-temperature-programmed reduction (H₂-TPR) data obtained from the calcined Ni_{0.5}Mg_{2.5}Al and Ni_{0.5}Ca_{2.5}Al catalysts are shown in Figure 17. The reducibility of the Ni-based catalysts

Figure 17. TPR results for the calcined Ni_{0.5}Ca_{2.5}Al and Ni_{0.5}Mg_{2.5}Al catalysts.

during the reduction process was an important factor in determining the level of reactivity since metallic Ni produced by the reduction process was in the active phase to initiate the reaction (e.g. CH₄ dissociation). The reducibility of the catalyst was affected by, and can be estimated by measuring, the strength of the interaction between the active phase and the support. The Ni_{0.5}Mg_{2.5}Al catalyst exhibited a small peak at low temperatures (<600 °C) and slightly increased at high temperatures (<700 °C) while the Ni_{0.5}Ca_{2.5}Al catalyst exhibited two reduction peaks at lower temperatures, 580 and 770 °C. Those two peaks can be assigned to complex NiO_x species corresponding to Ni/support interactions[39]. Since the Ni_{0.5}Mg_{2.5}Al catalyst did not exhibit any H₂ consumption until very high temperatures were reached (>750 °C), it was determined that the Ni_{0.5}Ca_{2.5}Al catalyst exhibited relatively free NiO species. Previous investigations confirmed that the reduction process for the NiO-MgO would be initiated at very high temperatures (>900 °C) since it produced a solid solution[26]. Additionally, the area under the TPR curve was clearly greater for Ni_{0.5}Ca_{2.5}Al than for Ni_{0.5}Mg_{2.5}Al and it can therefore be concluded that more Ni was reduced over the Ni_{0.5}Ca_{2.5}Al catalyst compared to the Ni_{0.5}Mg_{2.5}Al catalyst. This result also implied that the Ni_{0.5}Mg_{2.5}Al catalyst exhibited stronger interactions between the Ni and support since the reduction peaked at a higher temperature over the Ni_{0.5}Mg_{2.5}Al catalyst. These phenomena could be explained by comparing of the MgO, CaO, and NiO lattice sizes. Both MgO and CaO are face-centered cubic type oxides. However, only MgO has lattice parameters ($a = 4.2112$ Å) and bond distances ($A-B = 2.11$ Å) close to those of NiO ($a = 4.1946$ Å, $A-B = 2.10$ Å), with the lattice parameters and bond distances of CaO being $a = 4.8105$ Å and $A-B = 2.40$ Å[27]. This result suggested that NiO can be more easily substituted into the MgO lattice[24,28]. A catalyst that is more sus-

Figure 18. SEM of the fresh Ni_{0.5}Mg_{2.5}Al catalyst (100,000× magnification).

ceptible to reduction can ultimately provide more active sites on the catalytic surface, leading to higher reactivity. Based on the TPR results, the Ni_{0.5}Ca_{2.5}Al was the more reducible catalyst and had higher initial reactivity in the partial oxidation, CO₂ reforming and the oxidative CO₂ reforming of CH₄ processes relative to the Ni_{0.5}Mg_{2.5}Al catalyst, as shown in the reactivity data (Figure 3, Figure 4, and Figure 8). Additionally, since 720 °C was the reduction temperature used prior to the catalytic testing, the Ni_{0.5}Mg_{2.5}Al catalyst was only partially reduced.

SEM images of the fresh Ni_{0.5}Mg_{2.5}Al catalyst are shown in Figure 18, which display a layered structure (also referred to as a “card house” shape[15]) at the surface of the catalyst. Alternatively, the Ni_{0.5}Ca_{2.5}Al catalyst did not exhibit a layered structure [27]. This result corresponds with the XRD results (Figure 13), where the data indicated that the Ni_{0.5}Mg_{2.5}Al catalyst possessed a layered structure. Additionally, this layered structure provided stronger interactions between the active site (Ni) and the support (Mg-Al), resulting in a lower reducibility, as confirmed above.

3.2.3. Carbon deposition analysis

TPO experiments were performed to estimate the amount of carbon deposited on the catalytic surface after the reaction. The temperature of the catalyst bed was increased from 25 to 850 °C at a rate of 10 °C/min. Mass spectrometry (MS) was used to detect the carbon oxides formed, which was then used to determine the amount of carbon present. The amount of carbon deposited on the catalysts can be estimated by calculating the area under the TPO curves plotted in Figure 19. The amounts of carbon deposited are listed in Table 2 and confirm that the Ni_{0.5}Mg_{2.5}Al catalyst exhibited a significantly stronger resistance to coke formation relative to the Ni_{0.5}Ca_{2.5}Al catalyst. The resistance to coke formation might be related to the stronger interaction between Mg and Ni ions, which subsequently inhibited coke formation. Alternatively, the Ni_{0.5}Ca_{2.5}Al catalyst, which

Figure 19. TPO results for Ni_{0.5}Ca_{2.5}Al and Ni_{0.5}Mg_{2.5}Al catalysts after CO₂ reforming of CH₄ at 700 °C for 20 h.

Table 2. Amount of carbon deposition on the Ni_{0.5}Mg_{2.5}Al and Ni_{0.5}Ca_{2.5}Al catalysts after 20 h, CO₂ reforming at 700 °C.

Catalysts	Coke (wt%)	Reference
Ni _{0.5} Mg _{2.5} Al	2.9	This work
Ni _{0.5} Ca _{2.5} Al	11.9	
spc-Ni/Mg-Al	Trace	[18]
spc-Ni/Ca-Al	0.2	
Ni/MgO	5.2	[22]

was more easily reduced and resulted in Ni/Ca interactions being weaker, was more susceptible to deactivation via coke build-up.

SEM images of spent Ni_{0.5}Mg_{2.5}Al (Figure 20) and spent Ni_{0.5}Ca_{2.5}Al (Figure 21) catalysts after 20 h of CO₂ reforming of CH₄ at 700 °C exhibited significant differences in the carbon deposition traits. Using the Ni_{0.5}Mg_{2.5}Al catalyst resulted in significantly less carbon fiber evidence relative to the Ni_{0.5}Ca_{2.5}Al catalyst.

Figure 20. Spent Ni_{0.5}Mg_{2.5}Al catalyst after 20 h of CO₂ reforming of CH₄ (5,000 × magnification).

Figure 21. Spent $\text{Ni}_{0.5}\text{Ca}_{2.5}\text{Al}$ catalyst after 20 h of CO_2 reforming of CH_4 ($5,000\times$ magnification).

4. Conclusion

Different approaches for the synthesis gas production using Ni-supported catalysts have been investigated. The typical methods to produce synthesis gas (partial oxidation and CO_2 reforming of CH_4) by HT-like catalyst were performed for short and long reaction periods in order to investigate the effects of the structure of the catalyst on the stability and reactivity. Partial oxidation, CO_2 reforming and the oxidative CO_2 reforming of CH_4 processes to produce synthesis gas were evaluated at 700°C for 20 h in the presence of three different catalysts: $\text{Ni}_{0.5}\text{Mg}_{2.5}\text{Al}$, $\text{Ni}_{0.5}\text{Ca}_{2.5}\text{Al}$, and $\text{Ni}/\text{Al}_2\text{O}_3$. For the partial oxidation of CH_4 during 20 h of reaction, the $\text{Ni}_{0.5}\text{Mg}_{2.5}\text{Al}$, $\text{Ni}_{0.5}\text{Ca}_{2.5}\text{Al}$, and $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts exhibited similar levels of activity, which were close to the equilibrium levels, with the Ca- and Mg-containing samples exhibited no deactivation and the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst being deactivated. During CO_2 reforming of CH_4 , the $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{Ni}_{0.5}\text{Ca}_{2.5}\text{Al}$ catalyst conversions decreased as a result of coke formation, leading to deactivation of the catalyst. The $\text{Ni}_{0.5}\text{Mg}_{2.5}\text{Al}$ catalyst exhibited high and stable reactivities for over 100 h. The Oxidative CO_2 reforming of CH_4 , which combined the exothermic partial oxidation with the endothermic CO_2 reforming of CH_4 , can facilitate heat transfer between the reactions. The addition of O_2 reduced coke deposition on the catalysts since the oxygen can combust the surface carbon. Therefore, the catalytic activity levels for the partial oxidation and the oxidative CO_2 reforming of CH_4 processes could be maintained close to the equilibrium levels with less deactivation compared to the CO_2 reforming of CH_4 . The $\text{Ni}_{0.5}\text{Ca}_{2.5}\text{Al}$ catalyst exhibited the highest initial activity, but was deactivated quickly due to coke deposition. The $\text{Ni}_{0.5}\text{Mg}_{2.5}\text{Al}$ catalyst exhibited the most stable reactivity over 20 h of reaction. Additionally, the $\text{Ni}_{0.5}\text{Mg}_{2.5}\text{Al}$ catalyst exhibited excellent stability for the CO_2 reforming of CH_4 , even in the absence of oxygen in the feed gas. TPR data indicate stronger interactions between the Ni and Mg compared to that with

Ca, which seemingly correlates to catalyst stability in terms of decreased coke formation and subsequently allowing conversions and product yields to remain constant.

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