Ni/Ce-ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} 촉매의 첨가제에 따른 수소 및 합성가스 생성에 대한 실험적 연구

조원준\textsuperscript{1†}・유혜진\textsuperscript{1,2}・모용기\textsuperscript{1}・안화승\textsuperscript{2}
\textsuperscript{1}한국가스공사 연구개발원(KOGAS) DME기술연구센터, \textsuperscript{2}인하대학교 화학공학과

Experimental Study of Hydrogen and Syngas Production over Ni/Ce-ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} Catalysts with Additives

WONJUN CHO\textsuperscript{1†}, HYEJIN YU\textsuperscript{1,2}, YONGGI MO\textsuperscript{1}, WHASEUNG AHN\textsuperscript{2}
\textsuperscript{1}DME Technology Research Center, KOGAS, 960 Incheonshinhang-daero, Yeonsu-gu, Incheon, 406-840, Korea
\textsuperscript{2}Department of Chemistry and Chemical Engineering, Inha University, Yonghyun-dong, Nam-gu, Incheon 402-751, Korea

Abstract >> Performance tests on Ni/Ce-ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} catalysts with additives (MgO, La\textsubscript{2}O\textsubscript{3}) were investigated in the combined reforming processes (SCR, ATR, TRM) in order to produce hydrogen and carbon monoxide (it is called “syngas”). The catalyst characterization was conducted using the BET surface analyzer, X-ray diffraction (XRD), SEM, TPR and TGA. The combined reforming process was developed to adjust the syngas ratio depending on the synthetic fuel (methanol, DME and GTL) manufacturing processes. Ni-based catalysts supported on alumina has been generally recommended as a combined reforming reaction catalyst. It was found that both free NiO and complexed NiO species were responsible for the catalytic activity in the combined reforming of methane conversion, and the Ce-ZrO\textsubscript{2} binary support employed had improved the oxygen storage capacity and thermal stability. The additives, MgO and La\textsubscript{2}O\textsubscript{3}, also seemed to play an important role to prevent the formation of the carbon deposition over the catalysts. The experimental results were compared with the equilibrium data using a commercial simulation tool (PRO/II).

Key words : Combined reforming of methane(복합개질반응), SCR(Steam-CO\textsubscript{2} reforming, 수증기-이산화탄소 개질반응), ATR(Autothermal reforming, 자열개질반응), TRM(Tri-reforming, 삼중개질반응), Syngas(합성가스), Ni/Ce-ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} catalyst(촉매)

1. Introduction

In general, “synthetic fuel” refers to fuels manufactured via Fischer-Tropsch conversion, methanol to gasoline conversion or direct liquefaction. Conversion technologies in the commercial processes could be either direct conversion to liquid fuels or indirect conversion of the source substance initially to “syngas” which then goes through additional conversion process to make a liquid fuel. The growing attention to the production of syngas (H\textsubscript{2}/CO) is attributed to the convert of synthetic
fuel from natural gas, biomass, coal and/or coal base gas.

Synthesis gas or “syngas” is a mixture of hydrogen and carbon monoxide used as a major intermediary for the production of pure hydrogen or other chemical compounds. Syngas is manufactured industrially from hydrocarbon fuels either by steam reforming (SRM), catalytic partial oxidation (CPO), carbon dioxide reforming (CDR), autothermal reforming (ATR) or tri-reforming (TRM)\textsuperscript{[1-5]}. Steam reforming of hydrocarbons, in particular methane, is probably the most common and economical method for producing syngas in industrial scale. In this process, methane reacts with steam in the presence of a heterogeneous catalyst to produce hydrogen, carbon dioxide, and carbon monoxide. Though this process can yield high concentration of hydrogen (up to 70% on a dry basis), it is strongly endothermic. Hence, the reformer needs external heat to be supplied through the reactor wall to perform the fuel reforming, and consists of high capacity gas fired furnaces with a large number of parallel reactor tubes inside. The overall configuration of steam reformer with heat exchangers makes the reforming system very bulky and heavy.

To overcome the heat transfer problem in a steam reformer, the CPO has been often used as an alternative to produce hydrogen or synthesis gas from methane. The process is exothermic and can be easily started up upon ignition even without an aid of a catalyst. The temperature can be raised to over 1,000°C in the process which permits adiabatic operation and promotes SRM of the remaining species. However, CPO produces high carbon monoxide concentration. ATR combines the thermal effects of the SRM and CPO reactions by feeding the fuel, water, and air together into the reactor. The two processes occur simultaneously in the presence of catalyst in the reactor. The thermal energy generated from CPO is absorbed by SRM and, hence, the overall temperature is lowered, which is favorable to water-gas shift reaction to consume carbon monoxide and produce more hydrogen. Hence, the autothermal reformer is more compact and practical.

In recent years, the catalytic process of carbon dioxide reforming of methane into synthesis gas has attracted attention from many researchers for chemical utilization of the undesirable greenhouse gases: natural gas and carbon dioxide. This process produces synthesis gas with a H$_2$/CO ratio of about 1, which can be preferentially used for production of liquid hydrocarbons and oxygenates. Nevertheless, widespread implementation of this approach faces significant hurdles such as the problem of serious coking on the catalysts via the Boudouard reaction (2CO $\rightarrow$ C + CO$_2$) and/or methane decomposition (CH$_4$ $\rightarrow$ C + 2H$_2$).

TRM is a synergetic combination of CDR, SRM, and CPO of methane in a single reactor. The tri-forming concepts represents a new way of thinking both for conversion and utilization of CO$_2$ in flue gases without CO$_2$ separation and for production of industrially useful synthesis gas with desired H$_2$/CO ratios using flue gas or natural gas.

KOGAS has also developed and established a new innovative TRM technology since 2001\textsuperscript{[6]}. The combination of dry reforming with steam reforming can accomplish two important missions: to produce syngas with desired H$_2$/CO ratios and to mitigate the carbon formation problem that is significant for dry reforming. Integrating steam reforming and partial oxidation with CO$_2$ reforming could dramatically reduce or eliminate carbon formation on reforming catalyst thus increase catalyst life and
The typical catalyst for combined reforming process (SCR, ATR and TRM) is composed of the supported Ni catalyst with additives. It is important to develop and select the suitable Ni base catalyst because of sintering of Ni particle and carbon formation on the catalyst during the operation for producing the syngas in the combined reforming.

The objectives of this work is to investigate the catalytic performance of the Ni/Ce-ZrO$_2$/Al$_2$O$_3$ catalyst with the additives (MgO, La$_2$O$_3$) developed by us for the KOGAS combined reforming process.

2. Experimental

2.1 Preparation of catalysts

The catalysts were prepared by the following method. The loading amount of Ni was fixed to 9wt%. Ce-ZrO$_2$/Al$_2$O$_3$ support was prepared by the co-impregnation method. Cerium (III) acetate hydrate and zirconium nitrate were dissolved in distilled water with stirring 500rpm. This mixed solution was impregnated on $\alpha$-Al$_2$O$_3$. This material was calcined at 900°C for 6hr in air. The supported Ni catalyst was prepared by the impregnation using a solution of nickel (III) nitrate hexahydrate onto Ce-ZrO$_2$/Al$_2$O$_3$ support, followed by drying in microwave oven and calcining at 750°C for 6hrs in air. La$_2$O$_3$-promoted catalyst was prepared by the co-impregnation method using a aqueous soloution of nickel (III) nitrate hexahydrate and lanthanum nitrate hexahydrate on Ce-ZrO$_2$/Al$_2$O$_3$. MgO-promoted catalyst was also prepared by the same method. The prepared catalysts were denoted as Ni/Ce-ZrO$_2$/Al$_2$O$_3$, Ni-La$_2$O$_3$/Ce-ZrO$_2$/Al$_2$O$_3$ and Ni-MgO/Ce-ZrO$_2$/Al$_2$O$_3$ respectively.

2.2 Characterization

The BET surface area, total pore volume and average pore diameter of the catalysts were measured by nitrogen adsorption at -196°C using a BET instrument (Micromeritics, ASAP2020). About 0.05g of catalysts was used. The samples were pre-treated in high vacuum at 150°C to remove moisture and other adsorbed gases from the catalyst surface. X-ray diffraction (XRD, Bruker, D2Phase) patterns were recorded to investigate the crystal structure and compositional homogeneity of the prepared catalysts. The crystallite size was estimated by using the Scherrer equation. Temperature programmed reduction (TPR) experiments were carried out in an Autochem 2920 (Micromeritics). The sample of 50mg in a quartz reactor was pre-treated with He gas at 250°C for 1hr under He flow (50ml/min), cooled down to 50°C and then reduced using 10%vol H$_2$/Ar with a heating rate of 10°C/min from 50 to 1,000°C. A thermal conductivity detector was used to analyse the effluent gas after water trapping, and quantification of hydrogen consumption was carried out.

The morphologies of fresh catalysts were examined by scanning electron microscopy (SEM, Hitachi, S-4200). The quantitative analysis of coke amount on the used catalyst was performed with a thermogravimetry analyzer (TGA, NETZSCH, STA 409 PC). The sample of 20-40mg was heated from 30 to 1,400°C with a heating rate of 10°C/min in air.

2.3 Catalytic reaction

The methane reforming performance of the catalysts were investigated using a high pressure fixed-bed reactor system. The reactor with an inner diameter of 8mm was heated in an electric furnace a shown Fig. 1.
SCR, ATR and TRM reforming reactions were carried out at 900°C, 20 bar. For each run, 7.0g catalyst was loaded into a reactor. The ratio of CH$_4$/H$_2$O/CO$_2$ in the feed gas was kept to 1.0/1.6/0.9 in order to produce a proper ratio of H$_2$/CO to make reactants for Fischer-Tropsch reaction (F-T reaction), and the space velocity was about 4,000hr$^{-1}$ in SCR. In the ATR process, the ratio of CH$_4$/H$_2$O/O$_2$ was maintained as 1.0/1.0/0.8, and CH$_4$/H$_2$O/CO$_2$/O$_2$ was kept to 1.0/0.8/1.1/0.8 in the TRM process to make the suitable ratio of syngas. In the reactions, CH$_4$ feed flow rate was fixed to 150ml/min. The effluents from the reactor were analyzed on-line with a gas chromatograph (GC, Younglin, Autochro 2000) using a packed column (Porapak N) equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID).

The conversion of CH$_4$ and CO$_2$, the yield of H$_2$, CO, and H$_2$/CO ratio was calculated on the basis of the feed flow rates and the dry exit gas composition as obtained by gas chromatography using the following formulas:

\[
CH_4\text{ conversion (\%)} = \frac{[CH_4]_{\text{in}} - [CH_4]_{\text{out}}}{[CH_4]_{\text{in}}} \times 100
\]

\[
CO_2\text{ conversion (\%)} = \frac{[CO_2]_{\text{in}} - [CO_2]_{\text{out}}}{[CO_2]_{\text{in}}} \times 100
\]

\[
H_2\text{ yield} = \frac{[H_2]_{\text{out}}}{[CH_4]_{\text{in}}} \times 2 + \frac{[H_2O]_{\text{in}}}{[CH_4]_{\text{in}}} \times 100
\]

\[
CO\text{ yield} = \frac{[CO]_{\text{out}}}{[CH_4]_{\text{in}}} + \frac{[CO_2]_{\text{in}}}{[CH_4]_{\text{in}}} \times 100
\]

\[
H_2/CO\text{ ratio} = \frac{[H_2]_{\text{out}}}{[CO]_{\text{out}}} \times 100
\]

3. Results and Discussion

3.1 Catalyst characterization

Table 1 summarizes the characteristics of the catalysts prepared by the co-impregnation method. It shows the BET surface area, pore volume, and the size of Ni particles in the Ni/Ce-ZrO$_2$/Al$_2$O$_3$ and those with additives (La$_2$O$_3$ and MgO) catalysts.

The surface areas of the prepared catalysts were all in the range of 4.9-5.9m$^2$/g. Ni crystallites of the catalysts were also close but Ni-La$_2$O$_3$/Ce-ZrO$_2$/Al$_2$O$_3$ showed somewhat larger size than the others.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>surface area (m$^2$/g$^*$)</th>
<th>Ni crystallite size (nm$^*$)</th>
<th>Pore volume (cc/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Ce-ZrO$_2$/Al$_2$O$_3$</td>
<td>5.2</td>
<td>25.8</td>
<td>0.03</td>
<td>21.0</td>
</tr>
<tr>
<td>Ni-La$_2$O$_3$/Ce-ZrO$_2$/Al$_2$O$_3$</td>
<td>4.9</td>
<td>41.0</td>
<td>0.02</td>
<td>18.9</td>
</tr>
<tr>
<td>Ni-MgO/Ce-ZrO$_2$/Al$_2$O$_3$</td>
<td>5.9</td>
<td>30.3</td>
<td>0.06</td>
<td>23.2</td>
</tr>
</tbody>
</table>

$^*$Estimated from N$_2$ adsorption at -196°C.

$^*$Estimated from XRD
Fig. 2 XRD data of the catalysts prepared

The XRD patterns of the Ni/Ce-ZrO$_2$/Al$_2$O$_3$, Ni-La$_2$O$_3$/Ce-ZrO$_2$/Al$_2$O$_3$, and Ni-MgO/Ce-ZrO$_2$/Al$_2$O$_3$, are given in Fig. 2. The main phase of nickel in these catalysts was NiO that exhibited three major peaks at 2 theta values of 37.1°, 43.2° and 62.7°\cite{11}. For the La$_2$O$_3$-promoted catalyst, the characteristic reflections of lanthanum were present at 35.0°, 45.1°, 55.4°. For the Ni-MgO/Ce-ZrO$_2$/Al$_2$O$_3$ catalyst, MgO phase was detected to co-exists with NiO. It was difficult to distinguish clearly the MgO peak from the NiO peak because the peaks overlap each other\cite{12}.

The TPR patterns obtained for the catalysts prepared by co-impregnation method are shown Fig. 3. The temperature for free NiO reduction was 303°C\cite{13} or higher, depending on the additives. It is known that the peaks at lower temperatures are assignable to reduction of relatively free NiO species, whereas the peaks at higher temperatures are attributed to the reduction of complexed NiO species subjected to strong metal to support interaction (SMSI)\cite{14}.

In the case of Ni-La$_2$O$_3$/Ce-ZrO$_2$/Al$_2$O$_3$ catalyst, the peak detected at 426°C was attributed to reduction of species of lanthanum. In the case of Ni-MgO/Ce-ZrO$_2$/Al$_2$O$_3$ catalyst, the reduction peak at around 938°C peak could be assigned to reduction of complexed NiOx species\cite{15}.

The morphologies of the fresh catalysts were monitored by SEM analysis, as shown in Fig. 4. The fresh

![Fig. 2 XRD data of the catalysts prepared](image1)

![Fig. 3 TPR patterns of various catalysts](image2)

![Fig. 4 SEM images of various catalysts](image3)
Ni/Ce-ZrO₂/Al₂O₃ catalyst showed relatively uniform spherical particles with little agglomeration, whereas the fresh Ni-La₂O₃/Ce-ZrO₂/Al₂O₃ catalyst showed particles with a wide distribution of different particle sizes and shapes. Ni-MgO/Ce-ZrO₂/Al₂O₃ catalyst showed better dispersion of spherical particles than the La₂O₃-added catalyst[16].

3.2 Catalytic performance test

The prepared catalysts were tested for their catalytic activities in SCR, ATR and TRM at 900°C and 20bar condition. Fig. 5 shows CH₄ and CO₂ conversion and selectivities to H₂ and CO in respective processes. High CH₄ conversion and adequate syngas ratio were obtained over the Ni-La₂O₃/Ce-ZrO₂/Al₂O₃ catalyst, which showed the best performance among the catalysts tested in the SCR process. In the ATR Process, CH₄ conversion was 96.5% over Ni/Ce-ZrO₂/Al₂O₃ catalyst with the syngas ratio (H₂/CO) of ca. 2.0 suitable for F-T synthesis.

For DME production with TRM process, the syngas ratio was required to be 1.2±0.2. In the reaction test, Ni-MgO/Ce-ZrO₂/Al₂O₃ catalyst satisfied the required synthesis gas ratio and achieved the highest CH₄ conversion of 98.6%. Therefore, it is indicated that MgO as additive to the Ni/Ce-ZrO₂/Al₂O₃ is adequate for TRM process.

To evaluate the long term performance of the catalysts, the effectiveness of the catalysts was tested for 100 hr. As shown in Fig. 6, deactivation of catalysts Ni/Ce-ZrO₂/Al₂O₃ and Ni-La₂O₃/Ce-ZrO₂/Al₂O₃ occurred.
Ni/Ce-ZrO$_2$/Al$_2$O$_3$ catalyst showed higher activity and was stable for ATR process. Despite lower catalytic activity, Ni-La$_2$O$_3$/Ce-ZrO$_2$/Al$_2$O$_3$ was also relatively stable for 100hr. It is confirmed that Ni/Ce-ZrO$_2$/Al$_2$O$_3$ with added MgO shows the highest CH$_4$ conversion and stable activity in the long-term test. It is well established that selection of additives is important for enhancement in catalytic activity and stability in the mixed reforming process. The additives were effected to interact between NiOx species and support$^{[17]}$.

The carbon deposition on the used catalysts were monitored by TGA. Fig. 7 shows that all catalysts exhibited decreases in weight to around 400°C. This weight loss is a result of thermal desorption of water and CO$_2$ and to removal of easily oxidizable carbonaceous species$^{[18]}$. Ni-La$_2$O$_3$/Ce-ZrO$_2$/Al$_2$O$_3$ catalyst, on the other hand, exhibited a weight gain from 400°C to 500°C which is attributed to the nickel oxidation$^{[19]}$. It was shown that the TGA profiles for all three catalysts

---

**Fig. 7** TGA profiles of the used catalysts

**Fig. 8** Flow diagram for reactor modeling by Pro/II simulation program

**Fig. 9** Comparison of the simulation and experimental results((a) : SCR (b) : ATR (c) : TRM)
showed low weight losses afterwards due to graphitic carbon oxidized at high temperature\cite{20}.

Fig. 8 describes a process flow diagram for the reaction process of methane in this work simulated by the PRO/II simulation program to compare the experimental results with the equilibrium values. The simulated reaction processes assume a Gibbs reactor which models a chemical reactor by solving the heat and material balances based on minimizing the Gibbs free energy of the components in the reaction. Fig. 9 showed the comparison of the simulation with experimental results for conversion and H$_2$/CO ratio at 650-1000°C to cover the temperature ranges in SCR, ATR and TRM processes. It found that the conversion and H$_2$/CO ratio over these catalysts showed similar trends with the simulated values.\cite{21}

4. Conclusion

The effect on additives of Ni/Ce-ZrO$_2$/Al$_2$O$_3$ catalyst for the improvement of the catalytic activity and carbon tolerance in SCR, ATR and TRM processes of methane was investigated. The catalysts were prepared by co-impregnation using MgO and La$_2$O$_3$ as additives. In the SCR, high CH$_4$ conversion and acceptable synthesis gas ratio was achieved by Ni-La$_2$O$_3$/Ce-ZrO$_2$/Al$_2$O$_3$ catalyst, whereas Ni/Ce-ZrO$_2$/Al$_2$O$_3$ catalyst performed best for ATR process. In TRM process, MgO was more effective additive to activity and stability.

Acknowledgment

This study was supported by “Korea Gas Corporation R&D program” and “Ministry of Trade, Industry and Energy”.

References


