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Tri-reforming of CH_4 using CO_2 for production of synthesis gas to dimethyl ether

Seung-Ho Lee*, Wonihl Cho, Woo-Sung Ju, Byoung-Hak Cho,
Young-Chul Lee, Young-Soon Baek

LNG Technology Research Center, Research and Development Division, Korea Gas Corporation,
973, Dongchun-dong, Yeonsu-gu, Incheon 406-130, South Korea

Abstract

In general, there are three processes for production of synthesis gas; steam reforming, CO_2 reforming and partial oxidation of methane or natural gas. In the present work, we refer to tri-reforming of methane to synthesize syngas with desirable H_2/CO ratios by simultaneous oxy-CO_2-steam reforming of methane. In this study, we report the results obtained on tri-reforming of methane over the Ni/ZrO_2 based catalyst in order to restrain the carbon deposition and to evaluate the catalytic performance. Results of tri-reforming of CH_4 by three catalysts (Ni/Ce–ZrO_2, Ni/ZrO_2 and Haldor Topsoe R67-7H) are showed that the coke on the reactor wall and the surface of catalyst were reduced dramatically. It was found that the weak acidic site, basic site and redox ability of Ce–ZrO_2 play an important role in tri-reforming of methane conversion. Carbon deposition depends not only on the nature of support, but also on the oxidant as like steam or oxygen. Therefore, the process optimization by reactant ratios is important to manufacture the synthesis gas from natural gas and carbon dioxide.

Keywords: CO_2 abatement; Tri-reforming of methane; Carbon coke; Synthesis gas

1. Introduction

Natural gas conversion and utilization are important options for the new energy source. Recently, we have been made to convert methane, which is the main component of natural gas, into high valued hydrocarbon products [1,2]. In addition, a recent increase in papers concerning reforming of methane and partial oxidation of methane to manufacture synthesis gas has occurred in the past decade [3–6]. Moreover, the methane or natural gas reforming is one of the processes to produce synthesis gas with desired H_2/CO ratios for clean fuels and chemicals. In general, there are three processes for production of synthesis gas; steam reforming (SRM), carbon dioxide reforming (CDR) and partial oxidation (POM) of methane or natural gas. The catalytic reforming of methane with carbon dioxide to produce synthesis gas with lower H_2/CO ratio is a challenging approach for the chemical utilization of natural gas and carbon dioxide; consequently, considerable effort has been devoted to the development of high performance catalysts [7–9]

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \quad (\Delta H^\circ = 247.3\,\mathrm{kJ/mol}) \tag{1}$$

$$H_2O + CH_4 \rightarrow CO + 3H_2 \quad (\Delta H^\circ = 206.3\,\mathrm{kJ/mol}) \tag{2}$$

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* Corresponding author.

E-mail address: maruchi@kogas.re.kr (S.-H. Lee).

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$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \quad (\Delta H^\circ = -35.6\,\mathrm{kJ/mol}) \tag{3}$$

Ni/γ-Al_2O_3 catalysts have been used as the reforming catalysts of methane, theses catalysts have been developed to reach the highest thermal stability and activity for the methane reforming reaction. In our project, we have investigated POM over Ni/γ-Al_2O_3 with high activity as well as stability. However, in our experiment, Ni/γ-Al_2O_3 was not stable in SRM and CDR. Thus we have developed modified zirconia supported Ni catalysts for CDR, SRM and POM. We have shown that Ni/Ce–ZrO_2 precoated Al_2O_3 is highly active and stable in POM and SRM [10,11]. In present work, we refer to tri-reforming of methane with desirable H_2/CO ratios by simultaneous oxy-CO_2-steam reforming of methane for the bench scale process [12–14].

2. Experimental

Support materials employed in this study were γ-Al_2O_3 ($S_{BET} = 234\,m^2/g$) and θ-Al_2O_3 ($S_{BET} = 167\,m^2/g$), which was prepared by calcining γ-Al_2O_3 at 900 °C for 6 h. Ce–ZrO_2 modified θ-Al_2O_3 support was prepared by the incipient wetness method (CeO_2:ZrO_2:Al_2O_3 = 1:4:95, w/w). Supported Ni catalysts (3 wt.% Ni) were prepared by the impregnation method using appropriate amounts of $Ni(NO_3)_2\cdot 6H_2O$ onto supports followed by drying at 100 °C and calcining at 550 °C for 6 h in air [10].

All the reforming reactions (SRM, POM, CDR, and TRM) were carried out in a fixed-bed reactor, which made of an Inconel 800H alloy tube with dimension of 1.7 in. i.d. and 24 in. in length. The catalysts were reduced in the reactor with 5% (v/v) H_2/N_2 at 700 °C for 2 h before the reaction. The bench scale reforming systems were set up as shown in Fig. 1.

The conversion was calculated on the basis of the feed flow rates and the dry exit gas composition as obtained by gas chromatography. The conversion of methane and carbon dioxide were calculated as

$$\text{conversion of } CH_4 \text{ or } CO_2 = \frac{\text{moles of}\,(CH_4 \text{ or } CO_2 \text{ introduced} - CH_4 \text{ or } CO_2 \text{ in exit gas})}{\text{moles of } CH_4 \text{ or } CO_2 \text{ introduced}} \times 100$$

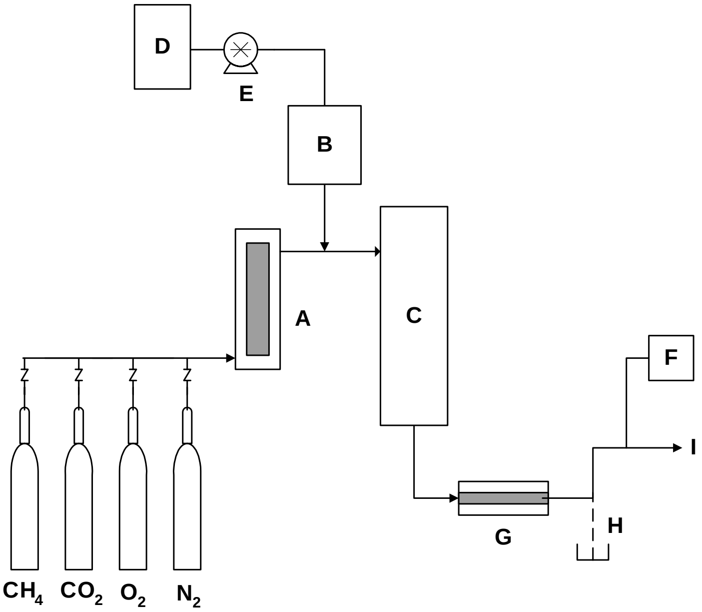

Fig. 1. Schematic diagram of experimental apparatus for CH_4 reforming. A: Feed pre-heater, B: steam generator, C: reactor, D: water, E: pump, F: gas chromatograph, G: cooler, H: drain, and I: vent.

3. Results and discussion

New catalyst design based on Ce–ZrO_2 support for the CO_2 reforming was sequentially prepared by the following steps: the modification of Ce–ZrO_2, the selection of a promoter on active Ni species, and simultaneous alteration of the support and Ni surface. According to previous report [15], Ni/Ce–ZrO_2 exhibited the highest activity in POM and SRM among the tested catalysts including Ni/MgO and Ni/$MgAl_2O_4$ which have been considered as the best catalyst in POM and SRM, respectively. Fig. 2 shows the CH_4 and CO_2 conversion with time on stream in CDR at 800 °C. Ni/Ce–ZrO_2 represented the highest activity as well as stability. CH_4 and CO_2 conversion were 92 and 93% after 20 h, respectively, with a H_2/CO ratio of 0.94. Ni/γ-Al_2O_3 and commercial catalyst of reforming, whose main component is Ni/MgO, however, deactivated with time on stream rapidly. Because of phase transformation of alumina, Ni/γ-Al_2O_3 has deactivated at high temperature. Otherwise, it seemed that the activity of commercial catalyst fade away due to carbon formation.

Fig. 3 shows the long-run test of Ni/Ce–ZrO_2 catalyst with time on stream in CDR at 800 °C. The presence of ceria in Ni/Ce–ZrO_2 catalyst has beneficial effects on the catalyst performance such as improving the catalyst stability and enhancing concentration of the highly mobile oxygen species. According to previous results, the role of ceria in this catalyst is assigned to form a thermally stable solid solution with zirconia and to give high capacity of oxygen storage. It is considered that the partially reduced ceria site produces active oxygen species by CO_2 dissociation, which reacts with the deposited carbon with the help of oxygen spillover from the support onto the Ni sites [11]. In consequence of reactions of synthesis of syngas, Ni/Ce–ZrO_2 catalyst appeared high activity as well as high stability in the CO_2 reforming.

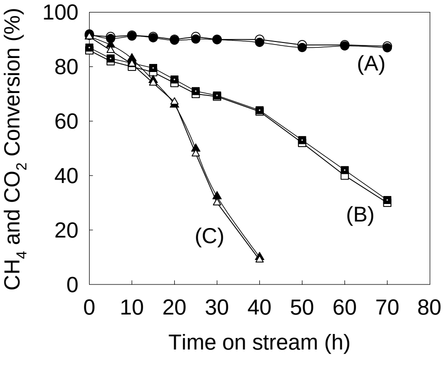

Fig. 2. CH_4 and CO_2 conversion with time on stream in CDR. (A) Ni/Ce–ZrO_2, (B) Ni/MgO, and (C) Haldor Topsoe R67-7H (reaction conditions: $CH_4/CO_2/N_2 = 1/1/1$, GHSV = 72 000 ml/h g, $T = 800$ °C, $P = 1$ atm, filled symbol: CH_4, open symbol: CO_2 conv.%).

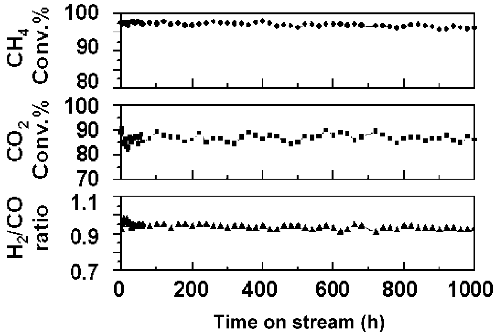

Fig. 3. Long-run test of Ni/Ce–ZrO_2 catalyst with time on stream in CDR (reaction conditions: $CH_4/CO_2/N_2 = 1/1.2/1$, GHSV = 10 000 ml/h g, $T = 800$ °C, $P = 1$ atm).

Figs. 4–6 show the experimental results for the effect of CO_2, H_2O ratio for the methane reforming reaction. From Fig. 4, it can be seen that CH_4

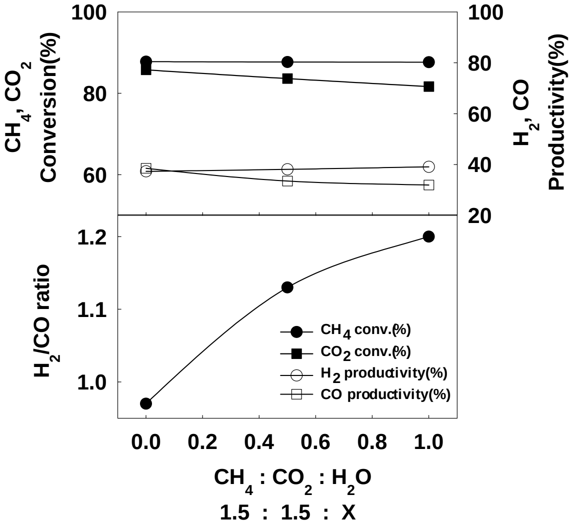

Fig. 4. Effect of steam on CO_2 reforming of methane over Ni/Ce–ZrO_2 catalyst (reaction conditions: catalyst loading = 1 kg, $T = 750$ °C, $P = 3$ atm).

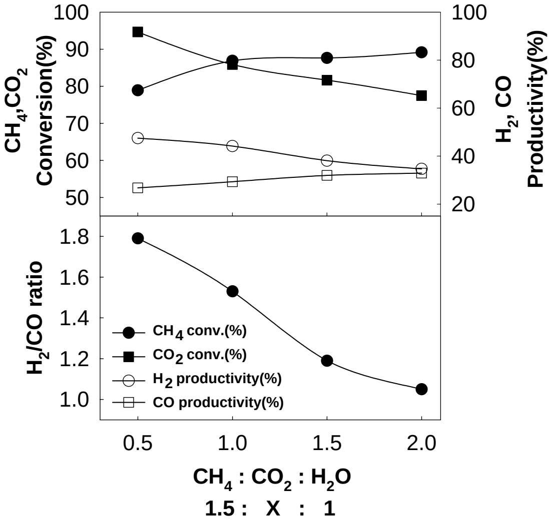

Fig. 5. Effect of steam on steam reforming of methane over Ni/Ce–ZrO_2 catalyst (reaction conditions: catalyst loading = 1 kg, $T = 750\,^{\circ}C$, $P = 3\,atm$).

conversion and H_2 productivity were slightly enhanced with increasing H_2O ratio but CO_2 conversion and CO productivity were reduced. Catalyst was deactivated by steam and water gas shift (WGS) reaction can reduce CO productivity. We fixed steam ratio to 1 and varied CO_2 ratio from 0.5 to 2. The results were shown in Fig. 5. The CH_4 conversion, CO productivity was slightly enhanced with increasing CO_2 ratio but CO_2 conversion and H_2 production were reduced. Fig. 6 shows the results for the effect of CO_2 addition into the reaction. As CO_2 flow rate was increased, H_2/CO ratio was decreased from 1.8 to 1 and conversion and productivity show similar trends as shown in Fig. 4.

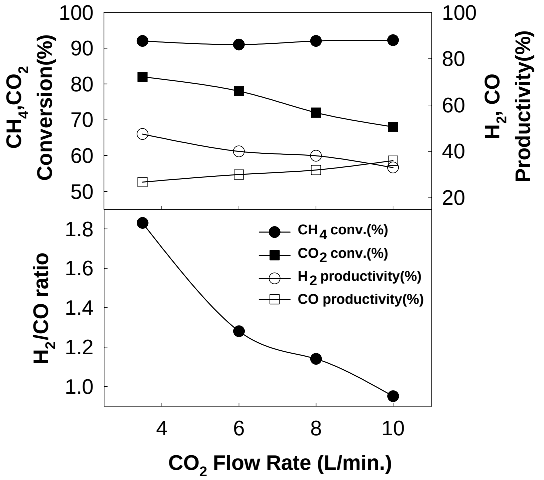

Fig. 6. Effect of CO_2 addition into the reaction for the mixed reforming over Ni/Ce–ZrO_2 catalyst (reaction conditions: catalyst loading = 1 kg, $T = 750\,^{\circ}C$, $P = 3\,atm$).

Table 1
Comparison of the activities among the four kinds of combined reforming reaction of methane; CDR, CDR and POM, CDR and SRM, and TRM

Reaction	$H_2O + O_2/CO_2$	X_{CH_4} (%)	X_{CO_2} (%)	H_2/CO ratio
(1) CDR	0.0	93.4	90.5	0.98
(2) CDR + POM	1.0	94.8	87.6	1.19
(3) CDR + SRM	1.0	96.5	85.3	1.35
(4) CDR + SRM + POM	2.0	95.6	82.3	1.44

Table 1 summarizes the reaction activities among the four kinds of combined reforming of methane over Ni/Ce–ZrO_2 catalyst at 800 °C. Tri-reforming reaction showed an efficient conversion of methane compare to other reactions; however, CO_2 conversion exhibited low reactivity for conversion around 82.3%. And then it was found a suitable ratio of H_2/CO (=1.44) for gaseous DME synthesis. In case of CDR, it showed a high conversion comparatively. However, it was found that a coking onto catalysts as well as difficult problems for temperature control due to generation of heat on real processes during reactions. Furthermore, the catalysts can be oxidized on steam easily on long time run. Thus, it can be seen that tri-reforming was one of the most promising approaches to the efficient process without coking deposition and generation of heat. Specially, it can be considered that the efficient process for chemical products from syngas with the suitable ratio of H_2/CO at a reasonable reactants ratio on reaction process.

4. Conclusions

The tri-reforming of CH_4 by Ni/Ce–ZrO_2 catalyst displays an excellent performance for the coke on the reactor wall and the surface of catalyst. It was found that the weak acidic site, basic site and redox ability of Ce–ZrO_2 play an important role in tri-reforming of methane conversion. Also, we optimized the ratio of methane, steam, carbon dioxide and oxygen for the syngas used DME process. The coke formation decreased rapidly by increasing steam molar ratio. Carbon deposition depends not only on the nature of support, but also on the oxidant as like steam or oxygen.

We obtained high efficient catalytic performances on Ni/Ce–ZrO_2 catalyst compared to commercial catalyst along with stability for production of syngas. From these founding, this catalyst can be attributed to the efficient catalyst for DME production process (50 kg per day) that is now under testing at our company.

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