

# DEVELOPMENT OF 50 KG/DAY DME PROCESS FROM CO<sub>2</sub> AND NATURAL GAS

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## 1. INTRODUCTION

South Korea has imported natural gas consisting mainly of methane since 1980s. Natural gas is considered to be not only the clean alternative to oil but the substance that can be transformed into more valuable resource. Recently various research efforts have been made to convert methane into high valued hydrocarbon products[1,2].

In recent years, Dimethyl Ether(DME) has received attention as an alternative fuel because of its cleanness and easiness to transportation [3,4]. DME produced from natural gas or coal bed methane is expected to play a role of securing energy supply and environmental conservation. At present, DME is used as a raw material for making chemicals and aerosol propellant such as hair spray, shaving cream to replace ozone-destroying chlorofluorocarbons. The properties of DME as fuel are sulfur free, rich in paraffin and extremely low aromatics. Also it has excellent solubility and fungibility compared with petroleum products. DME can be introduced at lower price than LPG, but it must be the first consideration before a DME project is launched to secure a certain volume of demand for the product.

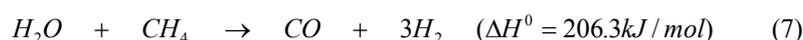
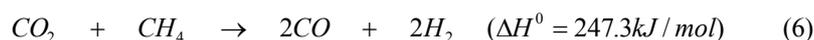
In general, DME is manufactured by a dehydration reaction of methanol. To utilize DME as an alternative fuel near the future, it must be produced at low cost in large quantities. Therefore, the recommendation process is the direct synthesis of DME from synthesis gas (syngas) which involves two steps, methanol synthesis followed by in situ methanol dehydration[5]. The reaction is reported to be consisted of three reaction step: these are methanol synthesis (1), methanol dehydration (2) and water gas shift (WGS) reaction (3).

Reaction formula	Reaction heat (kcal/mol-DME)
(1) $2\text{CO} + 4\text{H}_2 \rightarrow 2\text{CH}_3\text{OH}$	+43.4
(2) $2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$	+5.6
(3) $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	+9.8
(4) $2\text{CO} + 4\text{H}_2 \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$	+49.0
(5) $3\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_3\text{OCH}_3 + \text{CO}_2$	+58.8

Table 1. Reaction formula and reaction heat concerning DME synthesis

DME synthesis reaction depends mainly on both CO equilibrium conversion and the ratio of syngas, H<sub>2</sub>/CO. Syngas is potential raw material for chemical intermediates including both oxygenated

and hydrocarbon alternative fuels, octane enhancers, and a myriad of other industrial chemicals such as acetyls, alcohols, ethers, and olefins. In general, there are three processes for production of syngas; CO<sub>2</sub> dry reforming (CDR; Eq. 6), steam reforming (SRM; Eq. 7), and partial oxidation of methane (POM; Eq. 8) or natural gas. In present work we use tri-reforming of methane (TRM) to produce syngas with the suitable ratio of H<sub>2</sub>/CO by simultaneous oxy-CO<sub>2</sub>-steam reforming of methane [6.7].



In this study we report the results obtained on tri-reforming of methane over the Ni/ZrO<sub>2</sub> base catalysts in order to restrain the carbon deposition and to evaluate the catalytic performance. Also, we introduce the direct DME synthesis from syngas in a fixed bed type reactor and recent progress of 50kg/day DME production process.

## 2. SYNGAS SYNTHESIS FROM CO<sub>2</sub> AND CH<sub>4</sub>

### 2.1 Background

The catalytic reforming of methane with carbon dioxide to produce synthesis gas with lower H<sub>2</sub>/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. Although Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has been used as a reforming catalyst, it is necessary to modify the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support in order to obtain a thermally stable support for the reforming reaction. In our recent studies, we have successfully performed ORM over Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with high activity as well as high stability. However, Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was not stable in SRM and CDR. We have also developed modified zirconia supported Ni catalysts for CDR. In addition, we have shown that Ni/Ce-ZrO<sub>2</sub> is highly active and stable in POM and SRM. However, this system is difficult to commercialize due to the high price of Ce-ZrO<sub>2</sub>. [8,9] Therefore, in this work, we tried to precoat Ce-ZrO<sub>2</sub> onto a commercially available Al<sub>2</sub>O<sub>3</sub> support before impregnating Ni in order to decrease the Ce-ZrO<sub>2</sub> content and modify the  $\theta$ -Al<sub>2</sub>O<sub>3</sub> support. As a result, we have successfully developed Ni catalysts supported on Ce-ZrO<sub>2</sub> precoatd Al<sub>2</sub>O<sub>3</sub>. We report here that a novel catalyst, Ni/Ce-ZrO<sub>2</sub>/ $\theta$ -Al<sub>2</sub>O<sub>3</sub>, exhibited high catalytic performances in the tri-reforming reactions.

### 2.2 Experimental

Support materials employed in this study were  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (S<sub>BET</sub>= 234 m<sup>2</sup>/g) and  $\theta$ -Al<sub>2</sub>O<sub>3</sub> (S<sub>BET</sub>= 167

m<sup>2</sup>/g), which was prepared by calcining  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 900°C for 6 h. Ce-ZrO<sub>2</sub> modified  $\theta$ -Al<sub>2</sub>O<sub>3</sub> support was prepared by the incipient wetness method (CeO<sub>2</sub> : ZrO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> = 1 : 4 : 95 w/w). Supported Ni catalysts (3 wt% Ni) were prepared by the impregnation method using appropriate amounts of Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O onto supports followed by drying at 100°C and calcining at 550°C for 6 h in air.

All the reforming reactions (SMR, POM, CDR, and TRM) were carried out in a fixed-bed reactor, which made of an Inconel 800H alloy tube with dimension of 2" O.D., 1.725", and 24" in length. The catalysts were reduced in the reactor with 5wt% H<sub>2</sub>/N<sub>2</sub> at 700°C for 2 h before the reaction.

## 2.3 Results and Discussion

New catalyst design based on Ce-ZrO<sub>2</sub> support for the CO<sub>2</sub> reforming was sequentially proceeded by the following steps: the modification of Ce-ZrO<sub>2</sub>, the selection of a promoter on active Ni species, and simultaneous alteration of the support and Ni surface.

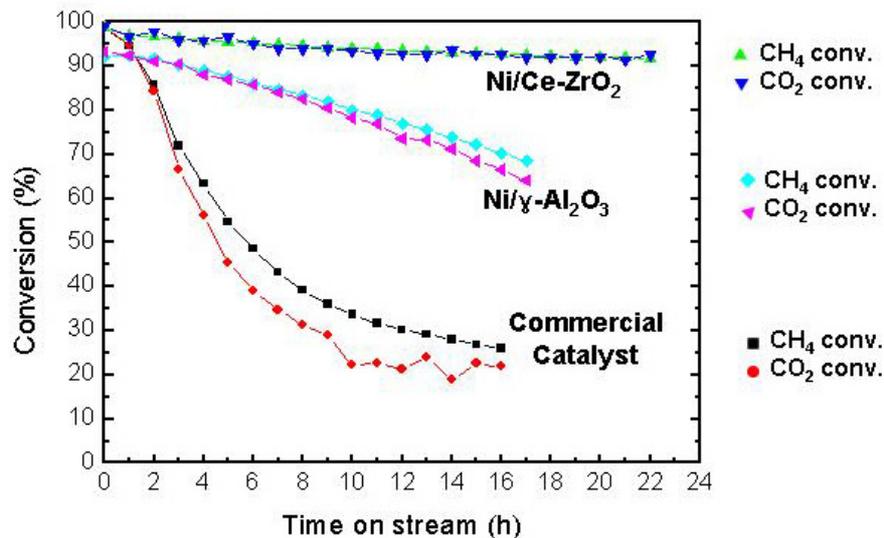


Figure 1: CH<sub>4</sub> and CO<sub>2</sub> conversion with time on stream in CDR (Reaction conditions: CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> = 1/1/1, GHSV = 72,000 ml/h.g, T = 800°C, P = 1 atm)

According to several reports[7], Ni/Ce-ZrO<sub>2</sub> exhibited the highest activity in POM and SRM among the tested catalysts including Ni/MgO and Ni/MgAl<sub>2</sub>O<sub>3</sub> which have been considered as the best catalyst in POM and SRM, respectively. Figure 1 shows CH<sub>4</sub> and CO<sub>2</sub> conversion with time on stream in CDR at 800°C. Ni/Ce-ZrO<sub>2</sub> represented the highest activity as well as stability. CH<sub>4</sub> and CO<sub>2</sub> conversion were 92 and 93% after 20 h, respectively, with a H<sub>2</sub>/CO ratio of 0.94. Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and commercial catalyst of reforming, which mainly component is Ni/MgO, however, deactivated with time on stream rapidly. Because of phase transformation of alumina, Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has deactivated at high temperature. Otherwise, it seemed that the activity of commercial catalyst fade away due to carbon formation.

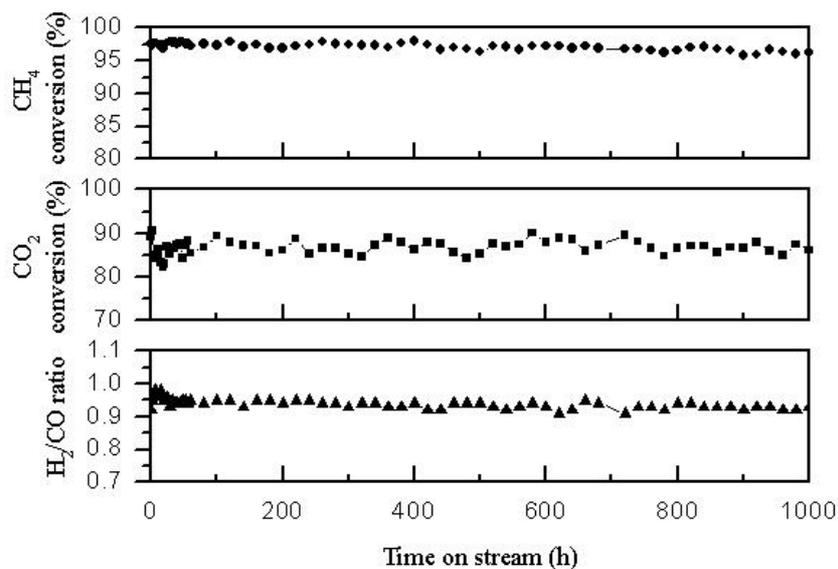


Figure 2: Long-run test of Ni/Ce-ZrO<sub>2</sub> catalyst with time on stream in CDR (Reaction conditions: CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> = 1/1.2/1, GHSV = 10,000 ml/h.g, T = 800°C, P = 1 atm)

Figure 2 showed long-run test of Ni/Ce-ZrO<sub>2</sub> catalyst with time on stream in CDR at 800°C. The presence of ceria in Ni/Ce-ZrO<sub>2</sub> 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<sub>2</sub> dissociation, which reacts with the deposited carbon with the help of oxygen spillover from the support onto the Ni sites[9].

In consequence of reactions of synthesis of syngas, Ni/Ce-ZrO<sub>2</sub> catalyst appeared high activity as well as high stability in the CO<sub>2</sub> reforming.

Reaction	H <sub>2</sub> O+O <sub>2</sub> /CO <sub>2</sub>	X <sub>CH<sub>4</sub></sub> (%)	X <sub>CO<sub>2</sub></sub> (%)	H <sub>2</sub> /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	1.05	95.6	82.3	1.44

Table 2: Comparison of the activities among the four kinds of combined reforming reaction of methane; CDR, CDR and POM, CDR and SRM, and TRM.

Table 2 summaries the reaction activities among the four kinds of combined reforming of methane over Ni/Ce-ZrO<sub>2</sub> catalyst at 800°C. Tri reforming reaction showed an efficient conversion of methane compare to other reactions, however, CO<sub>2</sub> conversion exhibited low reactivity for conversion around 82.3%. And then it was found a suitable ratio of H<sub>2</sub>/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.

### 3. DME PRODUCTION FROM SYNGAS

#### 3.1 Background

Recently, the process of direct synthesis of DME from syngas has received much attention during twenty years and researchers at Haldor Topsoe have developed a composite catalyst by the addition of specially treated H-ZSM-5 to the traditional  $Cu/ZnO/Al_2O_3$  methanol synthesis catalyst[10]. Some processes are known in which the DME synthesis is carried out in a single stage, by coupling a methanol synthesis to a dehydration catalyst, which is generally alumina. In the known processes, the methanol synthesis catalyst generally is a composition constituted by Cu, Zn and Cr or by Cu, Zn and Al, whereas the dehydration catalyst is generally alumina, solid acid catalysts.  $Cu/ZnO$  based catalysts were found to be effective towards methanol synthesis from CO hydrogenation[11-13]. Herein, we chose  $Cu/ZnO$  and  $\gamma-Al_2O_3$  system as the hybrid catalysts, i.e., combination of methanol synthesis and methanol dehydration to DME, in order to produce methanol and DME simultaneously.

#### 3.2 Experimental

The three hybrid catalysts were prepared by the mixing of two kinds of commercial catalysts methanol synthesis catalyst ( $CuO/ZnO/Al_2O_3 = 6:3:1$ ) and  $\gamma-Al_2O_3$  (strem chemicals, 97.7%). The hybrid catalysts (50g) were placed in a vertical fixed bed reactor (1.5 inch OD) and reduced by hydrogen (5% in nitrogen) in situ at 300□ for 3 h. The one step DME synthesis from syngas ( $H_2/CO = 1.5$ ) was performed under the reaction conditions of 30 and 50 atm, feed rate of 2000  $hr^{-1}$ , and the temperature of 250°C. The reactants were in situ analyzed by on-line GC (HP 6890: FID and TCD detector).

#### 3.3 Results and Discussion

Figure 3 shows the effect of  $H_2/CO$  ratio on carbon conversion (CO conversion) and product selectivity also represents the effect of reaction pressure and temperature. In a fixed bed reactor, the optimum conversion and selectivity was obtained at  $H_2/CO$  ratio of 1.5 at 250°C and 3.2MPa as shown in Figure 3 (a). It was exhibited a 30% conversion under  $H_2/CO$  ratio of 1.5 with 39.5% selectivity of DME, 9.6% that of methanol. Figure 3 (b) showed conversion as a function of temperature and pressure at  $H_2/CO=1.5$  over  $Cu/ZnO/Al_2O_3$ , methanol catalyst, and  $\gamma-Al_2O_3$ , dehydration catalyst.

Figure 3(b) suggests CO conversion increased around 42% at reaction conditions ( $T=280^{\circ}\text{C}$ ,  $P=5.3$  MPa). These results can be attributed that CO conversion increased with reaction temperature and pressure. On the other hand, this conversion has received maximum point due to a limited equilibrium reaction, and then, it is difficult to exhibit over 50% conversion and 30% yield of DME on the fixed bed reactor.

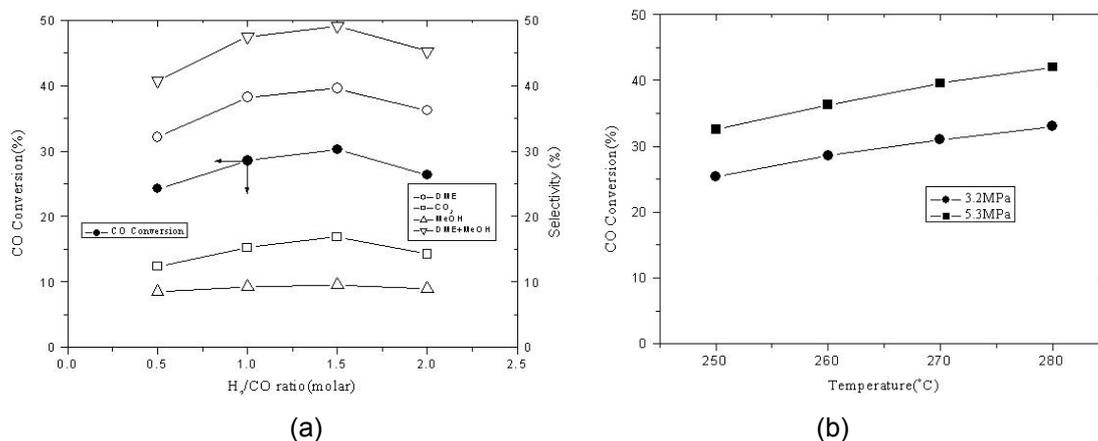


Figure 3: Conversion and selectivity by (a) the effect of  $\text{H}_2/\text{CO}$  ratio at  $260^{\circ}\text{C}$  and  $3.2\text{MPa}$  and (b) as a function of temperature and pressure at  $\text{H}_2/\text{CO}=1.5$ ,  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3 + \gamma\text{-Al}_2\text{O}_3$  catalyst

Among the examined catalysts, CuZnAl(developed at this work) and two kinds of commercial catalysts(HTCAI, ICCAI), commercial catalysts have been proven to be very active catalysts. Table 3 showed the selectivities of DME and methanol, and yield of DME, respectively. As shown table 3, ICCAI catalyst exhibited the highest CO conversion along with a lower yield. On the other hand, CuZnAl catalyst led to both the conversion around 31.5% and the selectivity around 44.7% with 5.34mol/kg-cat/hr also. From these founding, this catalyst can be attributed to the high chemical stability and the efficient catalyst for DME production process.

Catalyst	CO conversion (%)	Selectivity(%)		Space time yields DME (mol/kg-cat/hr) [methanol equivalent productivity]
		DME	CH <sub>3</sub> OH	
CuZnAl	31.5	44.7	2.6	5.34 [10.7]
HTCAI	28.6	48.3	6.7	4.93 [9.87]
ICCAI	34.0	20.2	59.7	2.14 [4.29]

Table 3: Comparison of the activities among three kinds of DME synthesis catalysts. (Reaction :  $P=5.3$  MPa,  $T=250^{\circ}\text{C}$ ,  $\text{H}_2/\text{CO}=1.2$ , space velocity= $2,000\text{hr}^{-1}$ )

#### 4. Outline of 50kg DME/day plant

The 50kg DME/day plant consisted of the synthesis of syngas by two step reforming reaction and single-step conversion process of syngas to DME. In the early this year (Jan. 2003), this plant was completed and went into operation at KOGAS LNG terminal site in Incheon. Test operation of the plant will be achieved in March of this year. KOGAS-led team will focus on marketing activities and will begin to develop markets for DME so that commercial operations can get under way as quickly as possible after technology development is completed.

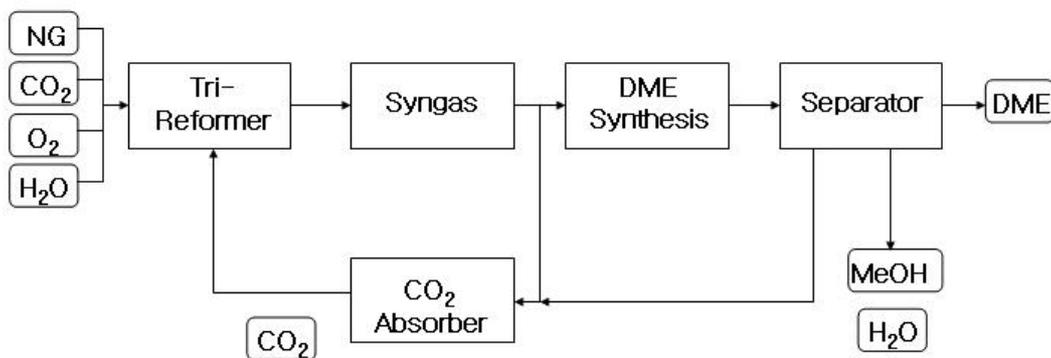


Figure 4: Process block diagram of 50kg DME/day production from CO<sub>2</sub> and CH<sub>4</sub>

Figure 4 shows the schematic process block diagram of 50kg DME/day plant. Syngas was synthesized over Ni/Ce-ZrO<sub>2</sub> catalyst with natural gas, CO<sub>2</sub>, O<sub>2</sub> and steam on tri-reforming reaction. During the reaction, produced the CO<sub>2</sub> was removed in absorber prior to the formation of DME, which was recycled. The syngas of H<sub>2</sub> and CO is introduced into reactor by using compressor for DME production, then, methanol and water were divided within separator. Both DME reformer plant for 50kg-per-day pilot plant and its reactor were fixed bed reactor. Before the tri-reforming reaction, pre-reformer was installed to obtain the C1 (methane) chemicals from natural gas. For the purpose of production of 50kg-per-day, the dimension of 7 tubular reactors was height of 1.2m and 1" I.D.

KOGAS has a target of fiscal 2006 for the start up of DME supplies. The final size of the operation will be determined from future feasibility studies, but is estimated at a five-ton-per-day pilot plant as an alternative to diesel automobile fuel, as a generator fuel in the power plants and as a fuel for fuel cell, and as a source of hydrogen energy

#### 5. Conclusion

Economic growth in the world has pushed up demand to the extent that the unbalance of energy supply and demand will be happened in the 21st century. The transportation, electric power, and other

energy related industries are facing a growing public demand for the reduction of the environmental load. DME is a clean and sustainable alternative fuel that can be produced from natural gas, coal or other organic resources through syngas. The properties of DME are suitable for the production of power generation fuel, transportation fuel and chemicals.

We obtained high efficient catalytic performances on Ni/Ce-ZrO<sub>2</sub> catalyst compared to commercial catalyst along with stability for production of syngas. In the DME synthesis process, CuZnAl catalyst contributed to the high conversion and selectivity with 5.34mol/kg-cat/hr. From these findings, this catalyst can be attributed to the high chemical stability and the efficient catalyst for DME production process.

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