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Studies on the steam and CO_2 reforming of methane for GTL-FPSO applications

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ABSTRACT

Steam CO_2 reforming (SCR) of methane for the production of syngas was simulated using PRO-II and investigated over Ni-based catalysts for GTL-FPSO applications. The Ni-based catalysts were prepared by an impregnation method. The catalysts before and after the reaction were characterized by N_2 physisorption, XRD and TEM techniques. The conversion of CH_4 was increased by increasing the concentration of H_2O and CO_2 in the feed. For the application in Co-based Fischer–Tropsch synthesis, the synthesis gas ratio of $H_2/CO = 1.85–2.0$ in the SCR was designed by the modeling of PRO-II simulator, and identified in a fixed bed reactor system by controlling the feed molar ratios of $CH_4:H_2O:CO_2$. It was found that Ni/MgO catalyst is more desirable catalyst for the production of synthesis gas than Ni/γ-Al_2O_3 and Ru/TiO_2 catalysts on the point of the low carbon formation and suitable H_2/CO ratio for the GTL-FPSO applications with Co-based FT process.

1. Introduction

Gas to liquids (GTL) technology attracts significant research interest due to high oil price since the last decade. GTL process is a good method to convert gaseous fuel to the synthetic liquid fuels [1]. Recently, the conversion of natural gas to synthetic fuel technology has attention because of many advantages of synthetic fuels [2]. GTL synthetic fuels prepared by Fischer–Tropsch (FT) synthesis contain extremely low sulfur and aromatic compounds [3,4]. GTL synthetic fuels also show low emission of carbon monoxide, nitrogen oxides, hydrocarbons, and other particulates [4]. Therefore, synthetic GTL fuel is regarded as a green fuel.

Production of synthetic fuels from natural gas involves two reactions. One is the conversion of natural gas to synthesis gas through reforming reaction, such as steam reforming [5], dry reforming [6], partial oxidation [7], and auto-thermal reforming [8]. The other is the conversion of synthesis gas to synthetic fuels through FT synthesis reaction over Fe- or Co-based catalysts [9]. It was known that Co-based catalyst shows high activity in low temperature FT synthesis and has long life, but it was needed H_2/CO mole ratio of 2. Thus, Co-based catalysts have been widely used as an efficient FT catalyst for GTL process [10].

In general, reforming processes such as steam reforming (SR) and carbon dioxide reforming of methane have some disadvantages, because both reforming reactions require an additional process to adjust the H_2/CO ratio [11]. In addition, partial oxidation (POX) of methane which meets the H_2/CO ratio of 2 creates difficulties in controlling the process because of the hot spots and explosion danger [12]. On the contrary, the steam CO_2 reforming (SCR) of methane is an available process for the direct control of the H_2/CO ratio which is suitable for the FT process by adjusting the feed molar ratio of steam and carbon dioxide [13].

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO, \quad \Delta H^{\circ}_{298} = 206\,\text{kJ/mol} \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H^{\circ}_{298} = -41\,\text{kJ/mol} \tag{2}$$

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO, \quad \Delta H^{\circ}_{298} = 247\,\text{kJ/mol} \tag{3}$$

Commercially, hydrogen is produced by the steam reforming of methane (Eq. (1)). It is usually followed by the water gas shift (WGS) reaction (Eq. (2)) so as to produce additional hydrogen. However, the presence of carbon dioxide in the feed can decrease the hydrogen productivity. The carbon dioxide reforming of methane is used to produce synthesis gas (Eq. (3)) [14].

Recently, GTL-FPSO (floating production storage and offloading) process has received much attention because of the possibility for application of stranded gas filed or associated gas in oil field. For the commercialization of GTL-FPSO, compact design of reforming

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Table 1
Simulation results estimated by PRO-II in the SCR of methane.

Feed molar rate (kmol/h)				Product molar ratio (kmol/h)					Reac. temp. (°C)	H_2/CO ratio	CH_4 con. (%)	CO_2 con. (%)
CH_4	H_2O	CO_2	H_2	CO	H_2O	CO_2	CH_4	C				
100	100	50	263.3	134.1	35.4	15.2	0.6	0	850	1.96	99.4	69.6
100	110	60	260.0	137.8	48.7	21.8	0.4	0	850	1.89	99.6	63.7
100	130	70	260.3	138.6	69.2	31.1	0.3	0	850	1.88	99.7	55.6
100	140	70	262.9	136.2	76.7	33.6	0.2	0	850	1.93	99.8	52.0
100	150	80	260.0	139.3	89.6	40.6	0.2	0	850	1.87	99.8	49.3
100	160	80	262.4	137.0	97.3	42.9	0.2	0	850	1.92	99.8	46.4
100	170	90	260.0	139.8	110.1	50.1	0.1	0	850	1.86	99.9	44.3
100	180	90	261.9	137.6	117.8	52.3	0.1	0	850	1.90	99.9	41.9
* **100**	**200**	**100**	261.5	138.2	138.3	61.8	0.1	0	**850**	**1.89**	99.9	38.2
100	100	60	257.0	137.0	40.2	21.4	1.6	0	800	1.88	98.4	64.3
100	110	60	260.0	134.4	47.1	24.3	1.3	0	800	1.93	98.7	59.5
100	120	70	258.6	137.5	59.4	31.5	1.0	0	800	1.88	99.0	55.0
100	130	70	261.7	134.9	66.6	34.3	0.8	0	800	1.94	99.2	51.0
100	140	80	259.8	137.9	78.9	41.7	0.7	0	800	1.88	99.3	47.9
100	150	80	262.6	135.1	86.3	44.3	0.6	0	800	1.94	99.4	44.6
100	160	90	265.2	132.7	93.7	46.8	0.5	0	800	2.00	99.5	48.0
100	170	90	263.1	135.2	106.0	54.4	0.4	0	800	1.95	99.6	39.6
100	170	100	258.6	140.0	110.6	59.8	0.4	0	800	1.85	99.6	40.2
100	190	100	263.5	135.2	125.8	64.5	0.3	0	800	1.95	99.7	35.5
* **100**	**200**	**100**	265.8	133.0	133.6	66.7	0.3	0	**800**	**2.00**	99.7	33.3

* Reaction feed condition

and FT process is desirable. It was reported that noble metals such as Pt, Pd supported catalysts and Ni based catalysts are active and noble for steam reforming, but they are susceptible to carbon formation [6,15,16]. However, the cost of noble metal-based catalyst is expensive, being the major drawback for their use in industrial applications. For that reason, Ni-based catalysts are generally the most used in reforming process of hydrocarbons either in laboratory or in industrial-scale [15,17]. It was considered that SCR of methane is desirable in the reforming process for GTL-FPSO application because H_2/CO ratio can be control by the optimization of feed [18,19].

In this work, the SCR of methane was simulated by PRO-II and investigated over Ni-based catalyst for application in GTL-FPSO process.

2. Experimental

2.1. Catalyst preparation

A commercial γ-Al_2O_3 supplied from Stream Chemicals (denoted as γ-Al_2O_3 (S), BET surface area = 221.8 m^2/g, pore volume = 0.49 cm^3/g) and a commercial MgO supplied from Sigma–Aldrich (denoted as MgO (S), BET surface area = 47.7 m^2/g, pore volume = 0.13 cm^3/g) were used as support. 20 wt% Ni-based supported catalysts were prepared by an impregnation method. Aqueous solution of nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] was added to each support. The impregnated samples were dried at 110 °C for overnight and calcined in a furnace in an air atmosphere by increasing the temperature from ambient temperature to 850 °C at a rate of 5 °C/min followed by keeping at 850 °C for 5 h.

A commercial TiO_2 supplied from Degussa (denoted as TiO_2 (S), BET surface area = 58.4 m^2/g, pore volume = 0.08 cm^3/g) was used as support. 2 wt% Ru/TiO_2 catalyst was prepared by an impregnation method. The impregnated sample was dried at 60 °C for overnight, and calcined at 350 °C for 5 h.

2.2. Catalyst characterization

The prepared catalysts before and after the reaction were characterized by N_2 physisorption, XRD and TEM techniques.

BET surface area of the catalysts was determined by N_2 adsorption at 77 K, using the physisorption analyser (Moonsorp-I, KIST, Korea). Prior to the measurements, the samples were pretreated in a vacuum condition at 573 K for overnight. X-ray diffraction (XRD) patterns were obtained using a Shimadzu XRD-6000 diffractometer with CuKα radiation. The Scherrer equation was used to calculate the metallic crystal size from the X-ray diffraction patterns. The physical and chemical properties of prepared catalysts are summarized in Table 1. TEM images were taken with a Tecnai G2 TEM.

2.3. Steam CO_2 reforming of methane

Fig. 1 shows the schematic diagram for SCR of methane. The SCR of methane was performed in a fixed bed reactor system. The preheater (0.008 m O.D. and 0.25 m length) and steam reforming

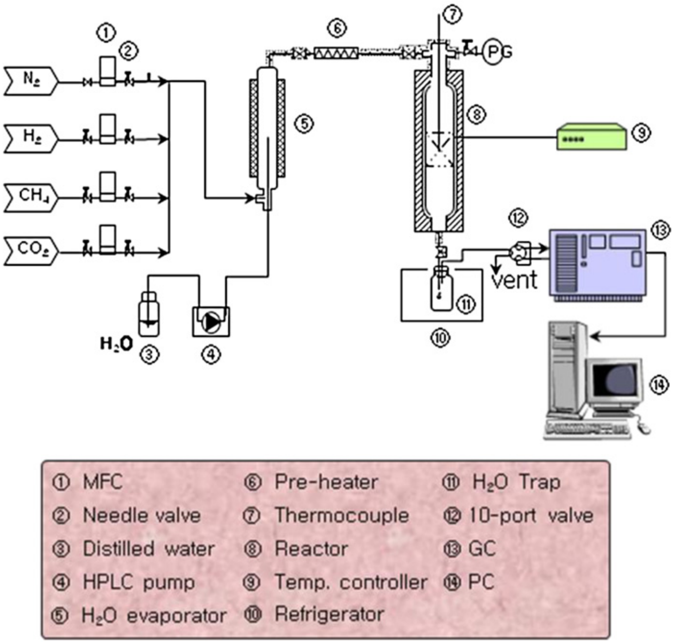


Fig. 1. Schematic diagram for steam CO_2 reforming of methane.

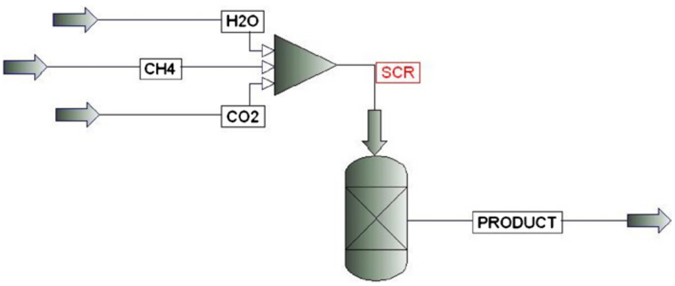


Fig. 2. Flow diagram for modeling a SCR reactor by PRO-II simulation program.

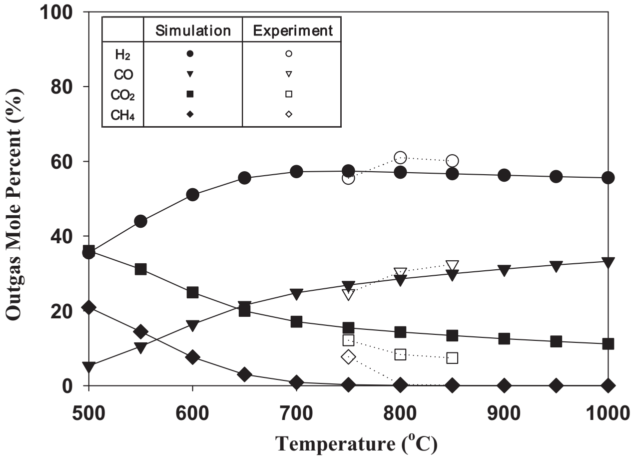
reactor (0.008 m O.D. and 0.25 m length) were made of an Inconel 600 tube, respectively [20]. Before the reaction, the Ni-based catalysts were reduced at 800 °C for 3 h in the hydrogen atmosphere. The flow rate of water feed was controlled by a liquid pump delivery, and the flow rates of CH_4 and CO_2 feeds were controlled by mass flow controller (MFC). The feeds were vaporized at 150 °C and preheated at 500 °C before being passed through the catalyst bed in the reactor. The unreacted H_2O was removed by a cold trap and then a gas effluent was analyzed by an on-line gas chromatograph (HP 7890A Series, TCD) and identified by a GC/MS (HP 7890A Series, MS detector). All runs were carried out at a temperature range of 650–850 °C, an atmospheric pressure, a space velocity of 10,000 h^{-1} and feed molar ratio of CH_4:H_2O:CO_2 = 1.0:2.0:1.0.

3. Results and discussion

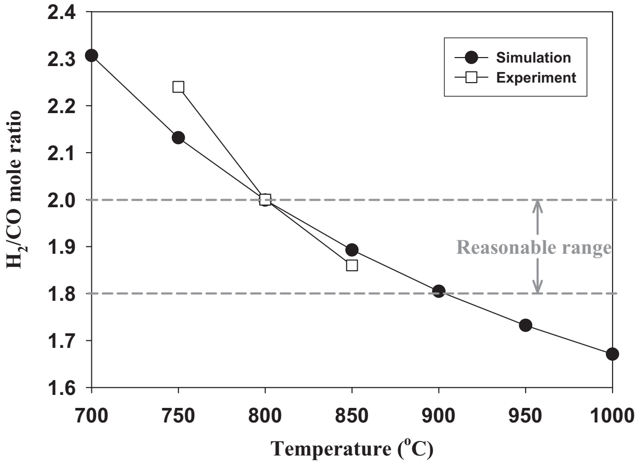
3.1. Simulation results

Fig. 2 describes the process flow diagram for SCR of methane simulated by PRO-II simulation. The SCR reactor uses Gibbs reactor which simulates a chemical reactor by solving the heat and material balances, based on minimizing the Gibbs free energy of the components in the reaction.

The Gibbs reactor determines the distribution of components which is expected at chemical equilibrium for the reaction system [21]. No prior knowledge of the chemistry of the system is required and the reaction stoichiometry need not be defined. All the components in the reactor are considered as reactants. The heat of reaction



(a) Product distribution



(b) H_2/CO mole ratio

Fig. 4. Comparison of the simulation and experimental results for the SCR of methane over 20 wt% Ni/MgO catalyst, showing the effect of temperature on (a) the outgas mole percent (b) the H_2/CO ratio (Feed molar ratio of CH_4:H_2O:CO_2 = 1.0:2.0:1.0). (a) Product distribution, (b) H_2/CO mole ratio.

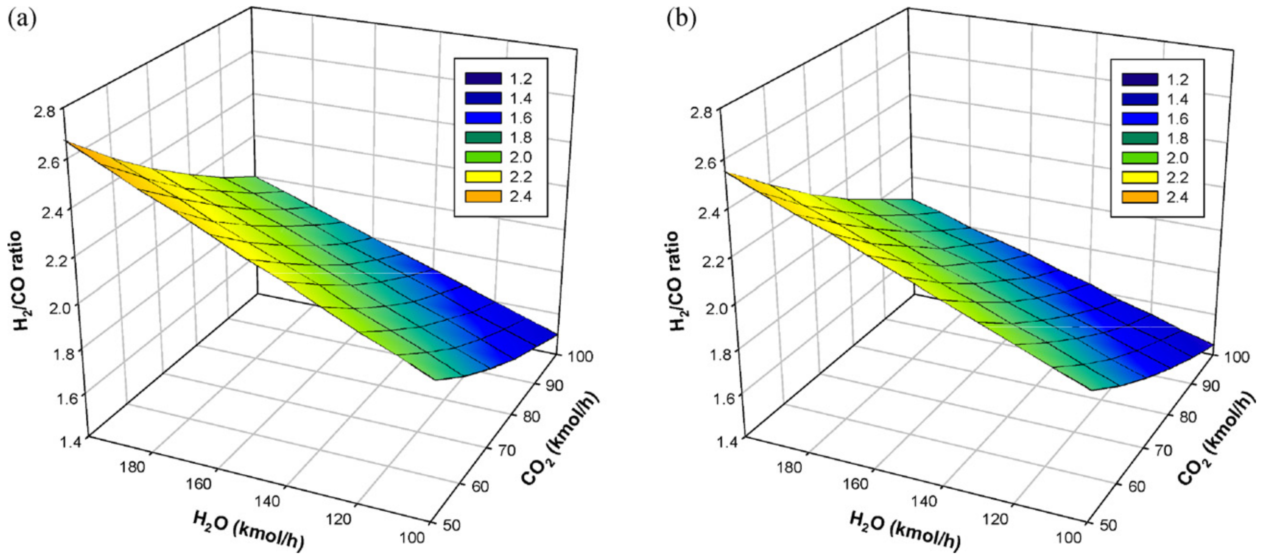


Fig. 3. The effect of feed molar ratio on the H_2/CO ratio produced in the SCR of methane at (a) 800 °C and (b) 850 °C. Operating condition: CH_4/H_2O/CO_2 = 100/100–200/50–100 kmol/h, 1 atm and 800–850 °C.

Table 2
Physical and chemical properties of prepared Ni-based catalysts.

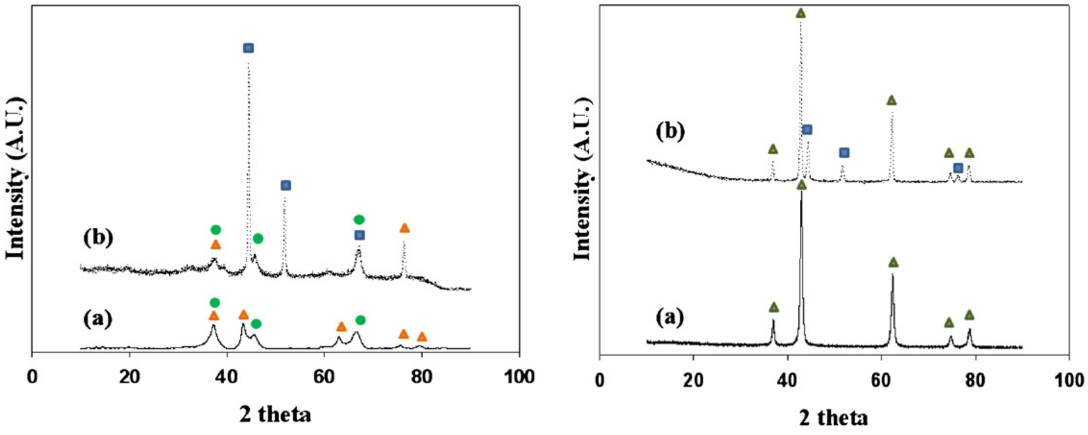
Catalyst	Metal loading (wt%)		BET surface area[a] (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	Ni particle size[b] (nm)
	Ni	Ru				
Ni/γ-Al_2O_3	20.0		81.2	0.13	8.1	13.3
Ni/MgO	20.0		42.9	0.08	6.7	25.3
Ru/TiO_2		2	34.3	0.08	9.8	–

[a] BET suface area was measured by N_2 physisorption.
[b] Ni particle size was calculated by XRD line broadening method.

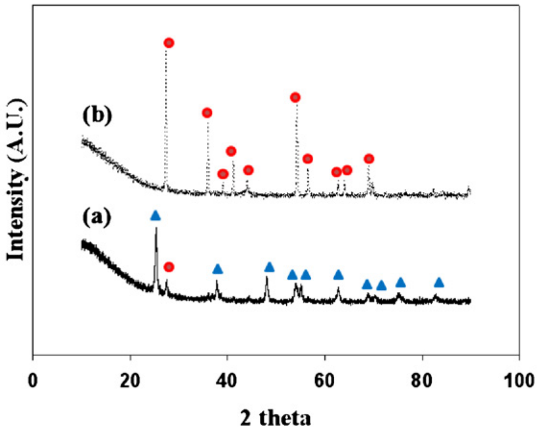
is calculated by PRO-II from heat of formation data. The heat of formation data must be entered for any non-library components in the reaction. The Gibbs reactor may use a VLE or VLLE method to determine the phase compositions for the product streams. In this work, Peng–Robinson method is used for estimation of physical properties of components species for the SCR of methane [21].

Methane supplied in SCR reactor is assumed to be fed with 100 kmol/h. The effect of temperature was investigated in the temperature range of 500–1000 °C, and 1 atm. Feed molar ratio was changed to the molar ratios of CH_4:H_2O:CO_2 = (1.0):(1.0–2.0):(0.5–1.0), respectively. The methane fed to the reformer is assumed to be 100 kmol/h and feed molar ratios of CH_4:H_2O:CO_2 were changed to find the optimum conditions for the product molar ratio of H_2/CO = 1.8–2.0 assuming Gibbs reactor for applications in Co-based FT process in GTL-FPSO system [22–24]. Table 1 shows simulation results for SCR of methane for GTL-FPSO process. The 132 cases were calculated in this simulation. Some cases were undesirable because of carbon formation, and/or low conversion of CH_4 and high reaction temperature. Only 20 cases showed H_2/CO product molar ratio of 1.8–2.0. We expected carbon formation in experiment and supplied excess steam. It was found that feed molar ratio of CH_4:H_2O:CO_2 = 1.0:2.0:1.0 is desirable for the application of Fischer–Tropsch synthesis in GTL-FPSO process using Co-based FT catalyst on the point of H_2/CO ratio, no carbon formation and high CH_4 conversion.

Fig. 3 shows the effect of feed molar ratio on the H_2/CO ratio produced in the SCR of methane at (a) 800 °C and (b) 850 °C, respectively. It was found that the H_2/CO ratio is depending on feed composition, and the H_2/CO ratio produced in the SCR of methane



(A) Ni / r-Al_2O_3 catalyst (B) Ni / MgO catalyst



(C) Ru / TiO_2 catalyst

Fig. 5. XRD patterns of catalysts before (a) and after (b) the reaction at 850 °C. (A) Ni/γ-Al_2O_3 catalyst (■ : Ni, ▲ : NiO, ● : γ-Al_2O_3), (B) Ni/MgO catalyst (■ : Ni, ▲ : $MgNiO_2$), (C) Ru/TiO_2 catalyst (● : TiO_2 (rutile), ▲ : TiO_2 (anatase)).

was increased with increasing the temperature from 800 °C to 850 °C.

Fig. 4 shows the comparison of the simulation with experimental results for the SCR of methane over 20 wt% Ni/MgO catalyst, showing the effect of temperature on (a) the outgas mole percent (b) the H_2/CO ratio. The PRO-II simulation was carried out by using Eqs. (1)–(3) in the SCR of methane with feed molar ratio of $CH_4:H_2O:CO_2 = 1.0:2.0:1.0$. It was found that the outgas concentration and the H_2/CO mole ratio in the SCR of methane over 20 wt% Ni/MgO catalyst showed similar trends with the simulation results within the range of experimental error. For the integration of the SCR of methane with Co-based FT reactor in the GTL process, the syngas of H_2/CO is needed because WGS reaction over Co-based FT catalyst did not occur for controlling H_2/CO mole ratio. It was found that the desirable reaction temperature is between 800 °C and 850 °C for the production of syngas with H_2/CO ratio of 1.85–2.0 in the SCR of methane for application GTL process. A small amount of carbon was formed under 800 °C. It may be considered that carbon was formed by the following exothermic reactions: Boudouard reaction (Eq. (4)), hydrogenation of carbon dioxide (Eq. (5)) and hydrogenation of carbon monoxide (Eq. (6)) [25].

$$2CO \leftrightarrow C + CO_2, \quad \Delta H^{\circ}_{298} = -172.4\,\text{kJ/mol} \tag{4}$$

$$2H_4 + CO_2 \leftrightarrow 2H_2O + C, \quad \Delta H^{\circ}_{298} = -90\,\text{kJ/mol} \tag{5}$$

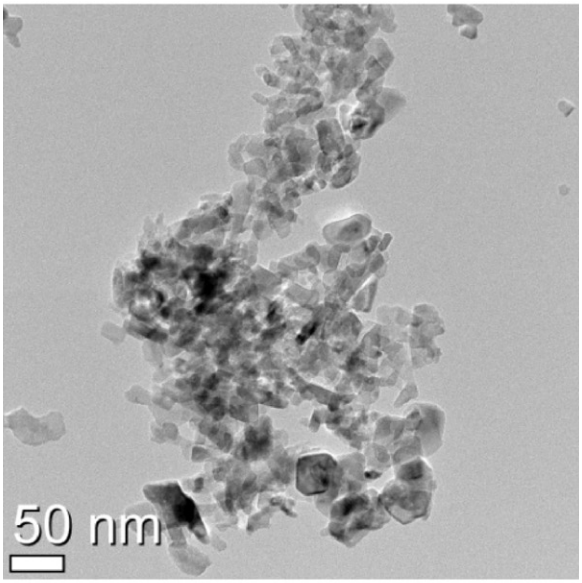
$$CO + H_2 \leftrightarrow H_2O + C, \quad \Delta H^{\circ}_{298} = -131.3\,\text{kJ/mol} \tag{6}$$

3.2. SCR of methane

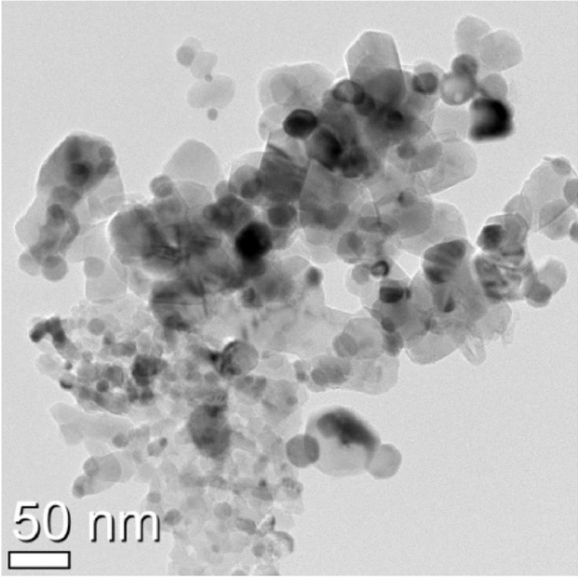
The physico-chemical and textural properties of the prepared catalysts are summarized in Table 2. BET surface area of Ni/γ-Al_2O_3, Ni/MgO and Ru/TiO_2 catalysts was measured by N_2 physisorption. It was found that Ni/γ-Al_2O_3 catalyst has higher BET surface area and pore volume than Ni/MgO and Ru/TiO_2 catalysts.

Fig. 5 shows XRD patterns of the catalysts before and after the SCR of methane at 850 °C. There are no major changes over Ni/MgO catalyst after the reaction. However Ni/γ-Al_2O_3 and Ru/TiO_2 catalysts showed major changes in the intensity and 2θ values. The Ni particle size was calculated from XRD line broadening method. It was found that the particle size of Ni over Ni/MgO catalyst was increased from 25.3 nm before the reaction to 39.2 nm after the reaction. It was identified that Ru/TiO_2 catalyst was changed from anatase phase into the rutile phase after the reaction of 850 °C for 30 h.

Fig. 6 shows TEM images of Ni/MgO catalysts before and after the SCR of methane at 850 °C. The Ni particle size of round shape was around 10–30 nm before the reaction. It was identified that the size of Ni particle was increased by the sintering after the reaction, as mentioned in Ni particle size measured by XRD method. It was found from XRD data that there was no NiC formation over used catalyst after the SCR reaction. The morphology of particles over Ni/MgO catalyst was slightly sintered after the reaction for 30 h.



(a) before the reaction



(b) after the reaction

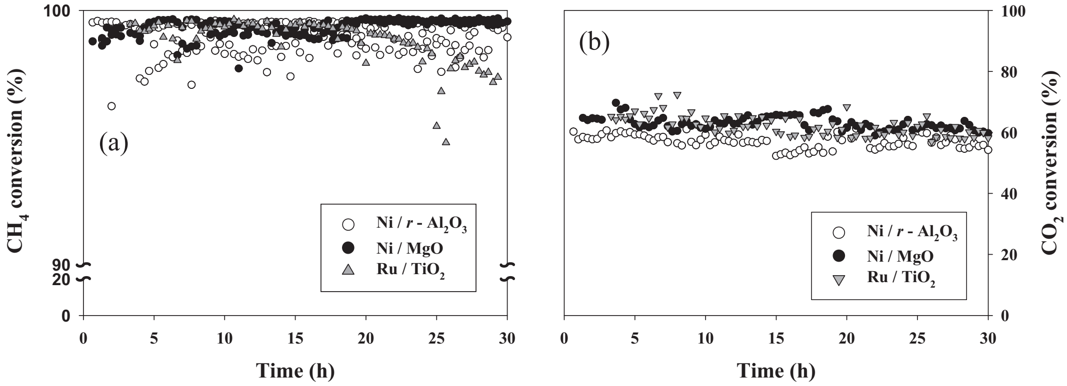
Fig. 6. TEM images of catalysts before (a) and after (b) the SCR over Ni/MgO catalyst at 850 °C.

Fig. 7 shows the (a) CH_4 conversion and (b) CO_2 conversion with a time on stream in the SCR of methane over Ni/γ-Al_2O_3, Ni/MgO and Ru/TiO_2 catalysts. Based on the results of simulation, the SCR of methane was carried out at 850 °C, feed molar ratio of $CH_4:H_2O:CO_2 = 1.0:2.0:1.0$ and GHSV of 10,000 h^{-1}. Most of CH_4 was converted with the CO_2 conversion of about 60%. The con-

Table 3

Results on the steam CO_2 reforming of methane over prepared catalysts.

Catalyst	Temp. (°C)	Conversion (%)			Outgas volume (%)			H_2/CO molar ratio	Total "Carbon Formation" (mg/g cat h)
		CH_4	CO_2	H_2	CO	CO_2	CH_4		
Ni/γ-Al_2O_3	850	99.37	57.13	63.11	28.87	7.91	0.13	2.19	–
Ni/γ-Al_2O_3	800	99.25	55.27	61.60	29.56	8.69	0.15	2.08	5.418
Ni/MgO	850	99.40	63.04	60.10	32.41	7.37	0.12	1.86	–
Ni/MgO	800	98.60	57.83	60.96	30.46	8.30	0.28	2.00	4.196
Ru/TiO_2	850	98.78	62.08	60.17	32.05	7.53	0.24	1.88	–



(a) CH_4 conversion

(b) CO_2 conversion

Fig. 7. Catalytic stability for steam CO_2 reforming of methane over Ni/γ-Al_2O_3, Ni/MgO and Ru/TiO_2 catalysts for 30 h. Reaction condition; feed molar ratio of CH_4:H_2O:CO_2 = 1.0:2.0:1.0, GHSV of 10,000 h^{-1}, temperature of 850 °C and pressure of 1 atm. (a) CH_4 conversion, (b) CO_2 conversion.

version of CH_4 over Ni/MgO catalyst was stable during the SCR of methane for 30 h. It was found that Ni/MgO catalyst showed higher catalytic activity and higher stability with a time on stream than Ni/γ-Al_2O_3 and Ru/TiO_2 catalysts under the tested conditions.

The reaction results on the steam CO_2 reforming of methane over Ni/γ-Al_2O_3, Ni/MgO and Ru/TiO_2 catalysts are summarized in Table 3. The product molar ratios of H_2/CO is 1.86–2.19 under the tested conditions. For GTL-FPSO application with Co-based FT process, the synthesis gas ratio of H_2/CO = 1.8–2.0 in the SCR of natural gas was required. There were no byproducts other than those listed in Table 3. It was found that carbon was formed at 800 °C over Ni/γ-Al_2O_3 and Ni/MgO catalysts. But carbon formation disappeared at 850 °C over both catalysts. Also, the Ni/MgO catalyst showed higher performance than Ni/γ-Al_2O_3 and Ru-TiO_2 catalysts on the point of low carbon formation and suitable H_2/CO ratio for GTL-FPSO application with Co-based FT process.

4. Conclusion

Steam CO_2 reforming of methane over Ni based catalyst was successfully carried out for the GTL-FPSO process application. The product composition was estimated by Pro-II simulation assuming Gibbs free energy minimization method. It was found that the feed molar ratio of $CH_4/H_2O/CO_2$ = 1.0/2.0/1.0 and reaction temperature of 800–850 °C are desirable for the production of the syngas with H_2/CO = 1.85–2.0 in the SCR of methane. It was also found that Ni/MgO catalyst is more desirable for the production of synthesis gas than the other catalysts on the point of the low carbon formation and suitable H_2/CO ratio for the GTL-FPSO applications with Co-based FT process.

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