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Effects of Re Additional and Co-fed Water Reactants on Bimetallic Ni-Fe Based Catalysts for Catalytic Partial Oxidation of Methane

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Abstract: The effect of Re addition on bimetallic Fe-Ni catalysts over γ-Al_2O_3 support for catalytic partial oxidation of methane was investigated at temperature range 650-850°C. It was observed that the presence of Re promoter can promote catalytic activity of Fe-Ni/Al_2O_3 particularly at 850°C. This was due to the presence of Re can enhance Fe-Ni dispersion, according to TPD-H_2 chemisorption measurement, which could efficiently reduce metal particle agglomeration and the growth of metal crystallites. Moreover, the effects of supports were also studied by comparing γ-Al_2O_3 and high surface area Ce-ZrO_2 supported Fe-Ni-Re catalysts. The Fe-Ni-Re/Ce-ZrO_2 exhibited not only an excellent performance towards CH_4 conversion (56.2%) and H_2 yield (68.7%) but also remarkable stability. Its better catalytic performance was mainly reasoned by the redox reactions between the absorbed CH_4 and the lattice oxygen on Ce-ZrO_2 surface also took place. Moreover, the effects of steam addition on Fe-Ni-Re/Ce-ZrO_2 performance were also carried out. With the presence of suitable H_2O content can further promote H_2 and CO yields as well as prevent the formation of carbon on the catalyst surface.

Keywords: Partial oxidation, Fe-Ni based catalyst, Re promoter, Ce-ZrO_2, hydrogen.

1. Introduction

Currently, fossil fuels are the energy sources most widely used worldwide today. However, fossil fuels are non-renewable. Moreover, pollutant emission during the combustion of fossil fuels has long made a serious impact on the climate change and environmental problem. Alternative fuels are one of the solutions to cut-off these problems. Alternative fuels, known as non-conventional or advanced fuels, are any materials or substances that can be used as fuels, other than conventional fuels such as fossil fuels, coal, or natural gas. Examples of some well-known alternative fuels include biodiesel, bioalcohol (methanol, ethanol, and butanol), wind energy, solar energy, geothermal energy, and hydrogen with fuel cell. In the recent years, the conversion non-fossil natural gas (or primarily the methane content of natural gas) into liquid fuels has gained increasing attention as a promising alternative for drop-in biofuel production. Commonly, liquid fuels made from gas are referred to as gas-to-liquid (GTL) fuels.

Gas-to-liquids (GTL) is a refinery process to convert natural gas, non-fossil natural gas, or other gaseous hydrocarbons (methane-rich gases) into longer-chain hydrocarbons or liquid synthetic fuels such as gasoline or diesel fuel [1]. The GTL process consists of three main technologies: reforming of synthesis gas (syngas) manufacture, FT synthesis, and product upgrading and/ or refining as in Figure 1.

Since the synthesis gas production is the most expensive step, there is great interest in optimizing routes for syngas production. In general terms, the catalytic partial oxidation (CPO) of methane is the reaction between methane and oxygen to obtain hydrogen and carbon monoxide (synthesis gas or syngas), represented by equation (1), methane is reacted with oxygen over a catalyst to yield syngas with H_2 to CO ratio near 2.

$$CH_4 + \tfrac{1}{2} O_2 \rightarrow CO + 2H_2 \qquad \Delta H = -38 \text{ kJ/mole} \quad (1)$$

The catalytic partial oxidation of methane (CPOM) to synthesis gas is normally catalyzed by Group VIII metals. Theoretical and experimental observations have demonstrated that catalyst activity is higher for noble metal-based catalysts, particularly Rh and Ru, followed by Ni, Os, Ir, Pt and Pd [2-3]. Rhodium (Rh) catalysts have been widely used in the CPO reaction. However, Rh has been the most expensive platinum group metal. Catalysts containing non-noble metals such as nickel (Ni) demonstrate good activity; however, coke formation and sintering during operation are a major drawback [4-6].

On the other hands, Ni catalyst has been wildly studied because of its high catalytic activity and economic advantages [7]. Most of the studies reported the catalytic performance can be improved by doping the promoter on catalyst. Therefore, modification of bimetallic catalysts it still feasible to develop as a new alternative catalyst by reducing carbon deposition as well as promoting catalytic activity and stability. Rhenium (Re) was an interesting promoter for this study since this catalyst has been recently reported to be a good promoter for Ni toward the high temperature reactions e.g. water gas shift reaction [8]. From the literature, adding small amount of Re reduced the Ni metal surface area and dispersion, which could be due to the strong interaction between Re and Ni atoms in Re-Ni structure [9]. As a consequence, in this work the effect of Re promoter doping on bimetallic Ni-Fe over different supports for catalytic partial oxidation of methane was carried out. Moreover, catalytic stability test and the effects of co-feed water were also investigated.

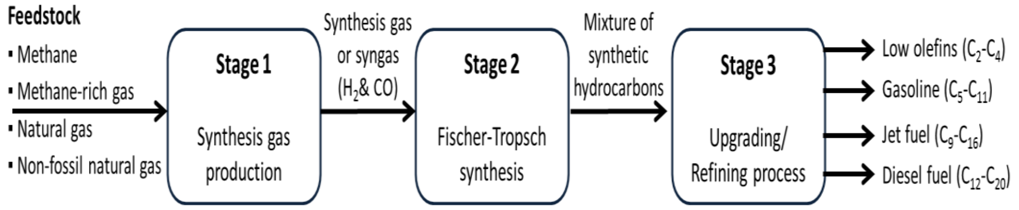

Figure 1. Schematic diagram of GTL production.

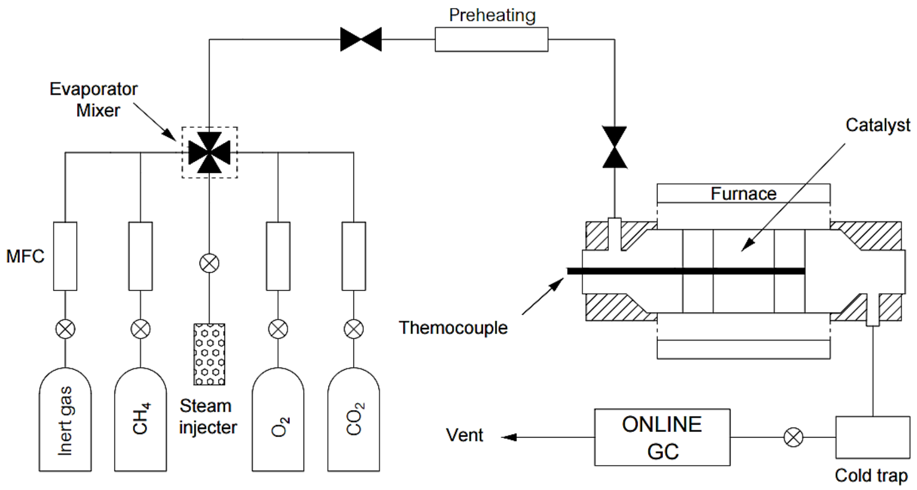

Figure 2 The schematic diagram of the experimental reactor for CPO.

2. Experimental

2.1. Catalyst synthesis

The catalysts for methane partial oxidation were prepared by impregnation technique on commercial γ-Al_2O_3 (Sasol company, Germany) and High surface area (HAS) Ce-ZrO_2 supports, which were prepared by the surfactant-assisted method. From previous works [10], to prepared Ce-ZrO_2 with weight ratio of Ce-Zr was 3/1, an appropriate cationic surfactant aqueous solution and 0.1 M cetyltrimethylammonium bromide solution from Aldrich were added to an 0.1 M aqueous solution containing $CeCl_3 \cdot 7H_2O$ and $ZrOCl_2 \cdot 8H_2O$ in a desired molar ratio. The mixture was stirred and then aqueous ammonia was slowly added with vigorous stirring. The mixture was continually stirred for 3 h, then sealed and placed in the thermostatic bath maintained at 90°C. After that, the mixture was cooled and the resulting precipitate was filtered and washed repeatedly with water and acetone.

For the preparation of catalysts precursor, calculated amount of required metal of iron (III) nitrate nonahydrate ($Fe(NO_3)_3 9H_2O$, Ajax Finechem), nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, Univar), and ammonium perrhenate (H_4NO_4Re, Sigma-Aldrich) were dissolved in deionized water. The prepared supports were then crushed and sieved to obtain 0.425 mm particle size then, impregnated with the metal aqueous solutions followed by drying overnight in an oven at 105°C and calcined at 600°C in air for 6 h.

2.2 Apparatus and Procedures

Figure 2 shows the schematic diagram of the experimental reactor system. The reaction was carried out in a fixed-bed stainless steel reactor with supplied gases. The supplied gas section consists of high purity gases of methane (CH_4, UHP grade 99.999%), oxygen (O_2, UHP grade 99.995%), and argon (Ar, UHP grade 99.995%) used as substances in this process. At the outlet of each gas cylinder, the pressure is controlled by mass flow controller to set the constant pressure of flow rate of inlet gases. Products from reaction (H_2, CO, CO_2, O_2 and CH_4) analyzed with online gas chromatograph (Shimadzu GC-2014, Japan) with and both thermal conductivity (TCD) and flame ionization (FID) detectors.

For catalytic testing toward the CPO process, a tubular quartz reactor was filled with catalyst about 100 mg. Inlet gases of methane and oxygen was introduced using CH_4/O_2 ratio is 2 in Ar dilution with total flow equal to 100 $cm^3 min^{-1}$. The studied reaction temperature was set and controlled by heater control in the range of 650-850°C with 10°C/min heating rate and held on for 5 mins to set the steady temperature before entered outlet gases into GC column. Before starting test reaction, the H_2 was fed into flow reactor for 3 hrs. to reduce metal oxide to metal form. The catalyst activity was defined and presented in terms of CH_4 and O_2 conversions and product (H_2, CO and CO_2) yields. The calculations were defined as equations (2)-(6).

$$X_{CH4} = \frac{F_{CH_4}^{in} - F_{CH_4}^{out}}{F_{CH_4}^{in}} \times 100\% \qquad (2)$$

$$X_{O2} = \frac{F_{O_2}^{in} - F_{O_2}^{out}}{F_{O_2}^{in}} \times 100\% \qquad (3)$$

$$Y_{CO} = \frac{F_{CO}}{F_{CH_4} + F_{O_2}} \times 100\% \qquad (4)$$

$$Y_{CO2} = \frac{F_{CO_2}}{F_{CH_4} + F_{O_2}} \times 100\% \qquad (5)$$

$$Y_{H2} = \frac{F_{H_2}}{F_{CH_4}^{in}} \times 100\% \qquad (6)$$

3. Results and Discussion

3.1 Catalytic activity toward partial oxidation of methane

Catalytic activity toward partial oxidation of methane was studied on 5%Fe-5%Ni/γ-Al_2O_3 compare with 4.5%Fe-4.5%Ni-1%Re/γ-Al_2O_3 at the temperature range between 650-850°C. The feed gases were introduced using CH_4/O_2 ratio of 2.0 in Ar balance. The variations in CH_4 and O_2 conversions as well as H_2, CO and CO_2 yields over catalysts are shown in Figure 3 and Table 1.

As shown in Figure 3 and Table 1, it can be seen that the catalytic reaction increases with increasing the temperature and achieved the best performance at high temperature 850°C. Among these two catalysts, in the present of Re as third metal exhibited the higher catalytic activity, from which CH_4 conversion and H_2 yield increased from 31.2% to 35.9% and 47.8% to 55.3%, respectively. In addition, CO yield from the reaction over Fe-Ni-Re/γ-Al_2O_3 was also higher than Fe-Ni/γ-Al_2O_3, while CO_2 yield was lower. It indicated trimetallic Fe-Ni-Re had better quality of synthesis gas produce. Particularly, from CO_2 formation over Fe-Ni catalyst can be noted that the reaction was more favorable to occur CH_4 complete oxidation, that is evident from the observation of higher O_2 conversion at the same operating temperature shown in Table 1. From experiment, it proved that the addition of Re (1%wt) over bimetallic Fe-Ni (4.5:4.5) was found to considerably improve the catalytic activity of Fe-Ni/γ-Al_2O_3. It was possible that the alloy phase formed during preparation was affected more active than the monometallic catalysts [11-12].

Moreover, TPO experiments were carried out to determine quantities of carbon deposited over both spent catalysts. It was found that less carbon was also observed on Fe-Ni-Re/γ-Al_2O_3 which reduced from 6.44 to 4.11 $mmol \cdot gcat^{-1}$. This indicated the better resistance toward carbon formation by the presence of Re, which was agreed with Yang, F., et al. [9] and Wang, L., et al. [12]. They reported the addition of Re over Ni as a promoter increased Ni dispersion through the strong interactions between Ni-Re and Fe-Re.

3.2 Effect of support types on its catalytic activity

In order to study the effect of support types on its catalytic activity toward partial oxidation of methane, the Ce-ZrO_2 support with optimum ratio (3:1) was chosen for comparison. The reaction temperature was increased from 650-850°C. Table 2 lists the CH_4 and O_2 conversions distribution over these two different supports. The CH_4 and O_2 conversion increased with increasing temperature. At 850°C, conversions reached maximum value over Ce-ZrO_2 catalysts by increased from 25.9% to 56.2% and 36.7% to 58.9%, respectively. As well as the results of products yields, which shows the presence of Ce-ZrO_2 can gain the highest of H_2 and CO yields were 68.7% and 54.3%, respectively. That can be reasoned by Ce-ZrO_2 surface has high ability to absorbed CH_4 and produce lattice oxygen [10]. Moreover, it was found that high surface area Ce-ZrO_2 presented greatly positive effect on the conversions and product yields in the presence of Re. From the reported by Chayakul K, and coworker [13], found that Re promoter can provide oxygen vacancies which encourage the redox properties on CeO_2 surface, so that increasing the reaction activity.

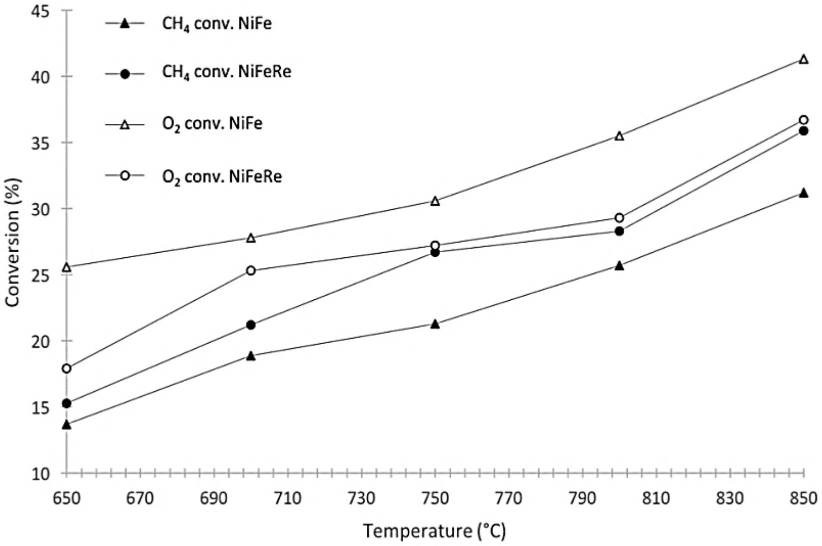

Figure 3. Conversion of CH_4 and O_2 over 5%Fe-5%Ni and 4.5%Fe-4.5%Ni-1%Re catalysts at 650-850°C.

Table 1. Product yield from partial oxidation of methane over Fe-Ni/γ-Al_2O_3 and Fe-Ni-Re/γ-Al_2O_3 catalysts as function of reaction temperature.

Catalysts	Temperature (°C)	Yield (%)		
		H_2	CO	CO_2
Fe-Ni/γ-Al_2O_3 (Fe:Ni = 5:5)	650	31.9	21.2	26.5
	700	35.6	24.6	31.3
	750	41.3	29.8	35.6
	800	43.9	28.7	38.9
	850	47.8	26.3	41.3
Fe-Ni-Re/γ-Al_2O_3 (Fe:Ni:Re = 4.5:4.5:1)	650	41.3	37.2	25.9
	700	43.6	39.7	29.7
	750	48.9	40.1	31.6
	800	51.4	43.9	32.9
	850	55.3	46.7	33.7

Table 2. CH_4 and O_2 conversion and product yield from partial oxidation of methane over Fe-Ni-Re/γ-Al_2O_3 and Fe-Ni-Re/Ce-ZrO_2 catalysts with different types of supports as function of reaction temperature.

Catalysts	Temperature (°C)	CH_4 conversion (%)	O_2 conversion (%)	Yield (%)		
				H_2	CO	CO_2
Fe-Ni-Re /γ-Al_2O_3 (Fe:Ni:Re = 4.5:4.5:1)	650	15.3	17.9	31.9	21.2	26.5
	700	21.2	25.3	35.6	24.6	31.3
	750	26.7	27.2	41.3	29.8	35.6
	800	28.3	29.3	43.9	28.7	38.9
	850	35.9	36.7	47.8	26.3	41.3
Fe-Ni-Re/Ce-ZrO_2 (Fe:Ni:Re = 4.5:4.5:1)	650	37.9	41.5	56.3	44.8	21.6
	700	42.9	46.8	57.6	48.2	24.8
	750	48.7	51.2	61.3	51.6	26.8
	800	52.3	55.6	65.8	55.1	28.3
	850	56.2	58.9	68.7	54.3	31.0

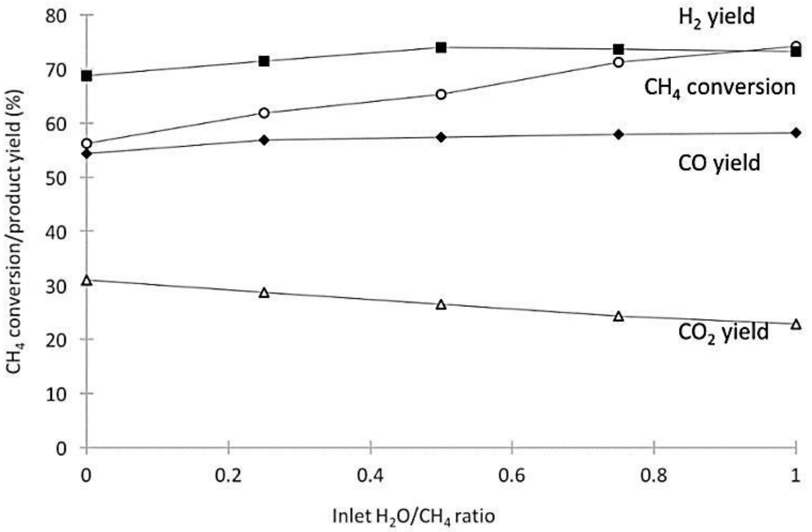

Figure 4. Effect of H_2O additional on CH_4 conversion and product yields from the partial oxidation of methane over Ni-Fe-Re/Ce-ZrO_2 catalyst at 800°C.

In addition, the amount of carbon deposition over the used catalysts was checked by the post-reaction TPO experiments. Comparison of carbon formation on catalysts surface after tested at 850°C shows in Table 3. The experiment detected highest amounts of carbon deposition on the surface of Fe-Ni/γ-Al_2O_3 followed by Fe-Ni-Re/γ-Al_2O_3 and Fe-Ni-Re/Ce-ZrO_2. This could be owning to the role of Re as stabilizer to prevent catalyst deactivation as previously reported [14]. Once more, in comparing between trimetallic catalysts on two supports, one can see that Ce-ZrO_2 indicated lowest coking than that γ-Al_2O_3. As a result, suggested a strong interaction between Ni atoms and Ce–ZrO_2 support made a good thermal stability and decrease the accumulation of carbon on the surface of Ni [15-16].

Table 3 Amount of carbon deposition on the surface of spent catalysts.

	Carbon formation (mmol·gcat^{-1})
Fe-Ni/γ-Al_2O_3	6.44
Fe-Ni-Re/γ-Al_2O_3	4.11
Fe-Ni-Re/Ce-ZrO_2	3.02

Furthermore, the percentage of metal dispersion of catalysts were performed by using temperature-programmed desorption (TPD) technique. Following Table 4 displays percentage of active metal dispersion through hydrogen chemisorption. By the H_2 was not chemisorbed on Re [8], so the data were referred to % active metal (Ni and Fe). As a consequence, the highest dispersion of Fe and Ni was found on Fe-Ni-Re/γ-Al_2O_3 because of high surface area of Al_2O_3 support. As well as presence of Re can help to disperse the metals and reduce cluster size of metal [8], which could also result in the improvement of catalytic activity. While the Ce-ZrO_2 support shows lower dispersion which reason by its properties that has less surface area than commercial Al_2O_3 [17].

3.3 Catalytic activity with co-fed steam

The unique high activity of the trimetallic Fe-Ni-Re catalyst over Ce-ZrO_2 support for CPO process is still attracted attention. Therefore, Ni-Fe-Re/Ce-ZrO_2 was selected for further studied by adding steam together with CH_4 and O_2 as autothermal reforming and operated at 800°C. The inlet H_2O/CH_4 molar ratios were varied from 0.25, 0.50, 0.75, to 1.0, with CH_4/O_2 molar ratio was kept constant at 2.0. Figure 4 illustrates the effect of H_2O concentration on the product composition at 800°C. It can be seen that the main products are similar to the partial oxidation (e.g., H_2, CO, CO_2). H_2 and CO yields were increased with increasing H_2O/CH_4 molar ratio until the ratio reached highest at ratio 0.50; then, steam becomes less pronounced at higher inlet H_2O/CH_4 molar ratio values. This could be due to adsorption competition between CH_4, O_2 and H_2O on the catalyst active sites [18].

Besides, the post-reaction TPO results, after being purged with helium, found that less quantities of carbon deposited were observed at high H_2O/CH_4 molar ratio. The addition of water was also beneficial because coke formation becomes unfavorable thermodynamic by carbon deposited were decreased from 3.02 mmol·g_{cat}^{-1} to 2.58, 2.21, 2.04, and 2.09 mmol·g_{cat}^{-1} in the presence of H_2O/CH_4 at 0, 0.25, 0.50, 0.75 and 1, respectively. Therefore, it is clear that the presence of H_2O shows desirable influence on the catalytic partial oxidation.

Table 4 Metal dispersion (%) of the catalysts.

	Metal dispersion (%)
Fe-Ni/γ-Al_2O_3	86.32%
Fe-Ni-Re/γ-Al_2O_3	89.47%
Fe-Ni-Re/Ce-ZrO_2	87.53%

4. Conclusions

The additional of Re are the good candidates to be used as the promoter for Fe-Ni catalysts for the catalytic partial oxidation of CH_4 particularly at high reaction temperature (650-850°C). From this work, the presence of Re can enhance Fe-Ni catalyst activity by improve their dispersion on the support, which can gain higher CH_4 conversion as well as H_2 and CO yields than bimetallic. The high surface area Ce-ZrO_2 supported Fe-Ni-Re was more suitable than Al_2O_3 for this reaction. It showed the excellent performance towards CH_4 conversion (56.2%) and H_2 yield (68.7%) and also remarkable stability. Its better catalytic performance was mainly reasoned by the TPO results that confirmed the higher resistance toward carbon deposition for Fe-Ni-Re/Ce-ZrO_2, owing to strong interaction between NiO and Ce-ZrO_2. In contrast, additional of H_2O content along with CH_4 and O_2 can promote H_2 and CO yields as well as reduces the amount of carbon deposition due to the occurring of steam reforming along with partial oxidation reaction.

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