Catalytic Activities of Ni and Cu Supported over Gd-CeO$_2$ toward Partial Oxidation of Methane

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Abstract: The catalytic partial oxidation of methane over Ni/GDC (Gd-doped CeO$_2$) and Cu/GDC was investigated at temperature range 400-650°C. It was found that Ni/GDC catalyst exhibited excellent performance towards CH$_4$ conversion and H$_2$ yield. On the other hand, Cu/GDC showed poor catalytic activity toward partial oxidation reaction because copper metal could promote complete oxidation reaction instead of partial oxidation reaction. Nevertheless, the coupling of Ni/GDC and Cu/GDC could increase H$_2$ yield from the reaction, which could be mainly due to the promotion of water gas shift reaction by Cu/GDC.

Keywords: Ni based catalyst; Cu based catalyst; GDC; Partial oxidation; Hydrogen.

1. Introduction

Methane is the principal component of natural gas. It is normally used as a fuel in the combustion engine. Although combustion is the easiest way to use natural gas, but this process also generate pollutant that is the cause of pollution problem. The conversion of methane into advance fuels or chemicals is an alternative way that can solve the pollution problem and also increase the product value [1].

Methane is normally converted into value-added product via synthesis gas route by using heterogeneous catalysts. Synthesis gas is the gas mixture of H$_2$, CO, and CO$_2$. Partial oxidation is the developed process which generates synthesis gas with ratio of H$_2$/CO = 2 as equation (1).which is suitable for Fischer-Tropsch reaction and methanol synthesis [2,3].

$$CH_4 + \tfrac{1}{2} O_2 \rightarrow CO + 2H_2 \qquad \Delta H = -22.2 \text{ kJ/mole} \qquad (1)$$

High conversion of methane and H$_2$ and CO selectivity can be obtained over noble metal (Pt, Rh, Pd and Ru) and transition metal (Ni, Fe and Co) catalysts. Ni-based catalysts are traditional catalyst for methane partial oxidation due to their low cost. However, sintering and coke formation on catalyst surface during operation are major drawback problem that needs to be solved. Moreover, presence of H$_2$O from the side reaction led to the decrease of hydrogen yield. Then, the catalyst for catalytic partial oxidation of methane should be developed [4,5].

CeO$_2$ or ceria have been widely studied as a catalyst supports for partial oxidation in the recent years because its high oxygen mobility can eliminate carbon formation. The fact that ceria can store and release oxygen seem to be the most significant property by the oxide shifting between CeO$_2$ and CeO$_{2-x}$ [6-10]. Ionic conductivity, which is the movement of an ion through the defects in the crystal lattice, is negligible in pure ceria because of no presence of defects in pure ceria structure. Conversely, high ionic conductivity can be obtained by the addition of rare earth metal or alkaline earth metal which can provided the defects to the ceria lattice [11].

The oxide of rare earth elements have been widely used as structural promoters to improve the activity, selectivity and stability of catalyst. When doping with lanthanide cations (i.e. Gd^{3+}, Y^{3+} and La^{3+}), an increase in the oxygen vacancies concentration in ceria structure is expected. Addition of lanthanide cations to ceria structure can promote the migration of oxygen ions through the lattice oxide and provides the material with high oxygen ion conductivity [12].

In this study, we report on the catalytic activity and selectivity of Ni-GDC (Gadolinium-doped ceria), Cu-GDC and the co-loading of transition metal with Re (rhenium) for catalytic partial oxidation of CH$_4$ in the temperature range of 400-650 °C at atmospheric pressure. Furthermore, we investigate the combination of Ni-based and Cu-based system to remove the water from gas product and maximize hydrogen yield via dual-catalyst bed system.

2. Experimental

2.1. Catalyst preparation

The catalysts for catalytic partial oxidation of methane were prepared by impregnation technique on commercial GDC (Gadolinia doped ceria, Daiichi, Japan) supporter with 10% Gd. The catalyst precursors were prepared by calculating the amount of required metal of nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O), ammonium perrhenate (Re(NO$_3$)$_3$) and copper nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O) and dissolving in deionized water. The metal aqueous solutions were impregnated to GDC followed by drying at 110°C overnight and calcined at 650°C in air for 6 h. The synthesized catalysts in this study were 5%Ni/GDC, 1%Re-4%Ni/GDC, 5%Cu/GDC, 1%Re-4%Cu/GDC and 1%Re-4%Ni-4%Cu/GDC.

2.2 Apparatus and Procedures

Figure 1 shows the schematic diagram of the partial oxidation system. The reaction was carried out in a fixed-bed tubular quartz reactor (OD 3/8 in, length 400 mm). The supplied gas section consists of high purity methane (CH$_4$, UHP grade 99.999%) and oxygen (O$_2$, UHP grade 99.995%) as reactants gas and argon (Ar, UHP grade 99.995%) as a carrier gas. At the outlet of each gas cylinder, the gas flow rate was controlled by mass flow controller to set the constant flow rate of inlet gases. The obtained gas products were analyzed by online gas chromatograph (Shimadzu GC-2014, Japan) with both thermal conductivity (TCD) and flame ionization (FID) detectors.
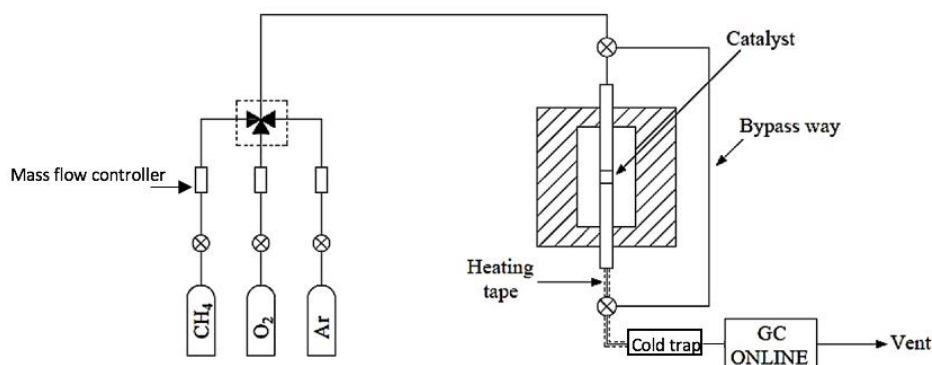
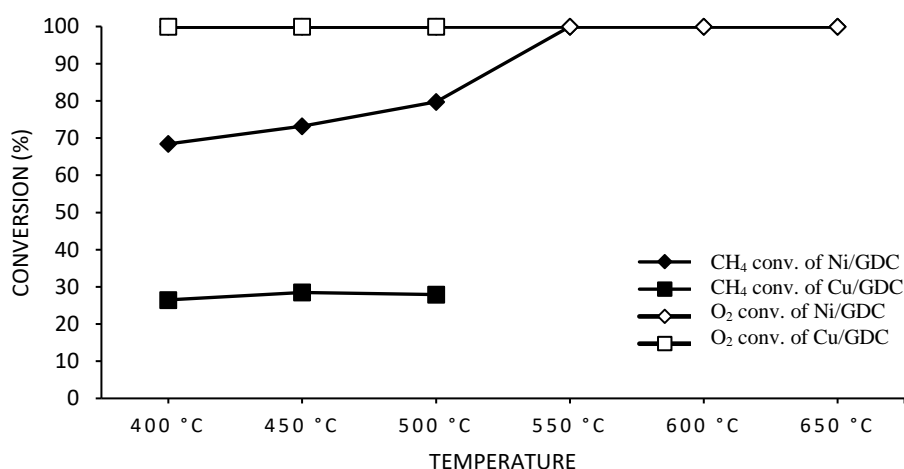**Figure 1.** The schematic diagram of the partial oxidation system.

Figure 2. Conversion of CH_4 over 5%Ni/GDC and 5%Cu/GDC catalysts at 400-650°C.

Prior the catalytic activities testing, 100 mg of catalysts were filled in the tubular quartz reactor and reduced at 400°C with H_2 (20% Vol. in Ar) for 2 hrs. The experiment was set and controlled by heater control in the temperature range of 400-650 °C at atmospheric pressure. The catalyst performance was evaluated in term of methane and oxygen conversion, product selectivity and product yield defined as equations (2)-(5).

% Conversion of methane $= \frac{CH_4 in - CH_4 out}{CH_4 in} \; x \; 100$ (2)

% Conversion of oxygen $= \frac{O_2 in - O_2 out}{O_2 in} \; x \; 100$ (3)

% Yield of hydrogen $= \frac{H_2 out}{CH_4 in \; x \; 2} \; x \; 100$ (4)

% Yield of CO or CO_2 $= \frac{CO \; out \; or \; CO_2 out}{CH_4 in} \; x \; 100$ (5)

3. Results and Discussion

3.1 Catalytic performance toward partial oxidation of methane

Catalytic performance toward partial oxidation of methane was studied on 5%Ni/GDC compare with 5%Cu/GDC at temperature range between 400-650°C. The inlet gas composed of CH_4 and O_2 with the ratio of 2.0 in Ar balance. The results were exhibited in terms of CH_4 and O_2 conversions as well as CO, CO_2 and H_2 yields as shown in Figure 2 and Table 1.

Table 1. Product yield from partial oxidation of methane over Ni/GDC and Cu/GDC catalysts as function of reaction temperature.

Catalyst	Temp. (°C)	Yield (%)		
		H_2	CO	CO_2
5%Ni/GDC	400	45.56	22.69	30.68
(0.1 g)	450	48.88	25.99	33.47
	500	53.15	30.59	27.27
	550	57.53	42.11	32.64
	600	56.45	41.89	32.37
	650	56.49	42.32	32.80
5%Cu/GDC	400	0.51	0	32.20
(0.1 g)	450	0.29	0	30.59
	500	0.41	0	30.75

As shown in Figure 2 and Table 1, Ni/GDC catalyst displayed good performance in terms of conversion, H_2 yield, and H_2/CO ratio whereas Cu/GDC showed poor catalytic activity. The catalytic activity in terms of CH_4 conversion and hydrogen yield over Ni/GDC catalyst increased with the increasing of the temperature. The highest CH_4 conversion is 57.53% and the highest hydrogen yield is 57.53% which achieved at 550 °C. In fact, the increasing of the reaction temperature should increase the CH_4 conversion and hydrogen yield, however, CH_4 conversion and hydrogen yield, which obtained at 600-650°C, could be limited by the presence of H_2O and the thermodynamic equilibrium of the partial oxidation reaction resulted in the decrease in CH_4 conversion and hydrogen yield while increasing the reaction temperature. When compared this result with the literature data [5], it can be suggested that metallic nickel active site is better than nickel oxide active site in term of CH_4 conversion

and H_2 yield as suggested by Zhu et al [2]. The doping of Gd in ceria structure showed better catalytic performance than ceria supporter in terms of CH_4 conversion, hydrogen yield, CO yield and CO_2 yield [4].

Although the doping of Gd in ceria structure can promote the partial oxidation reaction, but Cu/GDC catalyst shown the promoting effect on complete oxidation reaction which converted CH_4 and O_2 into CO_2 and H_2O by the catalyzing of Cu active site resulted in low CO and H_2 production.

3.2 Catalytic partial oxidation of methane over dual bed catalyst

From the literature [13], Cu/GDC showed good catalytic activity in water-gas shift reaction resulted in the increase of hydrogen yield. In this section, Ni/GDC catalyst was combined with Cu/GDC catalyst in dual bed catalyst system as shown in Figure 3 to eliminate H_2O from the gas product and increase hydrogen yield via water-gas shift reaction. 50 mg of each catalyst were filled in the same reactor and used to study in catalytic partial oxidation at temperature range between 400-650 °C.
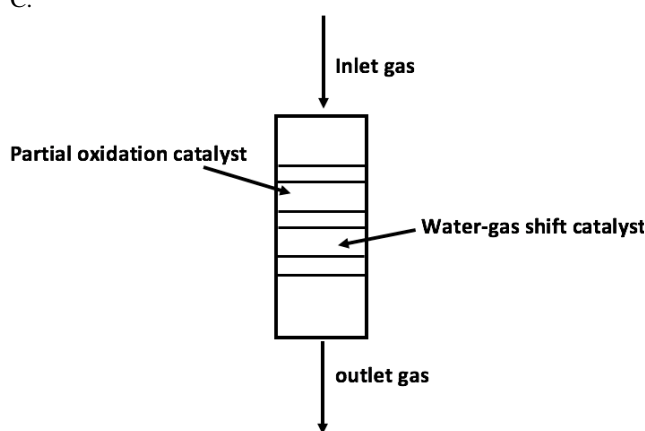

Figure 3. Reactor diagram of dual bed catalyst system.

The results of dual bed catalyst, which consists of the first partial oxidation catalyst layer (Bed 1) and the second water-gas shift catalyst layer (Bed 2), are presented in Table 2. It can be seen that CH_4 conversion increased with the increase of temperature and reached 100% at 600 °C with 60.10% hydrogen yield.

Table 2. CH_4 and O_2 conversion and product yield from partial oxidation of methane over Ni/GDC- Cu/GDC dual bed system as function of reaction temperature.

Catalyst	Temp. (°C)	% Conversion		% Yield		
		CH$_4$	O$_2$	H$_2$	CO	CO$_2$
5%Ni/GDC	400	72.67	100.00	52.97	27.49	29.08
(0.05 g) and	450	75.13	100.00	56.91	30.77	27.80
5%Cu/GDC	500	81.18	100.00	60.78	37.29	23.86
(0.05 g)	550	87.42	100.00	67.32	45.07	19.52
	600	100.00	100.00	60.10	39.65	38.80
	650	100.00	100.00	56.92	38.60	38.24

When compared the result with the single catalyst section as shown in Table 3, the experiment of dual catalyst experiment had higher conversion in the temperature range of 400-500 °C. The reason could due to the occurring of steam reforming by the catalysis of Cu/GDC catalyst [14]. Conversely, it showed lower CH_4 conversion at 550 °C because of insufficient amount of Ni/GDC catalyst in the catalyst bed. However, hydrogen yield of dual catalyst experiment was higher than Ni/GDC catalyst at all temperature. It means that H_2O was converted into H_2 from water-gas shift reaction by Cu/GDC catalyst.

Table 3. Comparison of results of dual bed system and Ni/GDC experiment as function of reaction temperature.

Catalyst	Temp. (°C)	% Conversion		% Yield		
		CH$_4$	O$_2$	H$_2$	CO	CO$_2$
5%Ni/GDC	400	68.44	100.00	45.56	22.69	30.68
(0.1 g)	450	73.19	100.00	48.88	25.99	33.47
	500	79.77	100.00	53.15	30.59	27.27
	550	100.00	100.00	57.53	42.11	32.64
	600	100.00	100.00	56.45	41.89	32.37
	650	100.00	100.00	56.49	42.32	32.80
5%Ni/GDC	400	72.67	100.00	52.97	27.49	29.08
(0.05 g) and	450	75.13	100.00	56.91	30.77	27.80
5%Cu/GDC	500	81.18	100.00	60.78	37.29	23.86
(0.05 g)	550	87.42	100.00	67.32	45.07	19.52
	600	100.00	100.00	60.10	39.65	38.80
	650	100.00	100.00	56.92	38.60	38.24

4. Conclusions

Ni/GDC showed excellent performance toward partial oxidation of methane, from which high CH_4 conversion (100%) and H_2 yield (57.53%) can be achieved. The coupling of Ni/GDC and Cu/GDC could further increase H_2 yield from the reaction, which could be mainly due to the promotion of water gas shift reaction by Cu/GDC.

Acknowledgements

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