Comparison of the Catalytic Performance of Ni/CeO$_2$/ZrO$_2$ and Commercial Catalyst during Steam Reforming of Methane

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Catalytic performance and characterization of Ni/CeO$_2$/ZrO$_2$ and commercial catalyst from Indonesia were investigated in steam reforming of methane. Ni/CeO$_2$/ZrO$_2$ catalyst was prepared using co-impregnation of cerium nitrate and nickel nitrate onto zirconia support material. BET, SEM, EDS, XRD, TPD, TG, and ICP analyses were employed for the characterization of the catalysts.

Remarkable catalytic performance of Ni/CeO$_2$/ZrO$_2$ catalyst at 600°C operating temperature and atmospheric pressure of about 74.9% methane conversion was obtained compared to 55.9% using the commercial catalyst. In addition, the presence of cerium in Ni/CeO$_2$/ZrO$_2$ was effective in improving the stability and resistance to coke formation. Less carbon formation was confirmed from the thermo-gravimetric analysis. These results showed that the prepared catalyst is promising in the industrial application which can be used at lower operation temperature for energy saving.

Keywords: Steam reforming, Methane, Ni/CeO$_2$/ZrO$_2$, *and* Carbon formation

INTRODUCTION

Steam reforming of CH$_4$ is a widely-practiced technology for syngas production. In the industry, the process is usually carried out at high temperature conditions, using nickel-based catalysts on alumina support.

The principal reactions for converting methane into hydrogen are [1]:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$(-\Delta H°_{298} = 206 \text{ kJ/mol}) \quad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2$$
$$(-\Delta H°_{298} = -41 \text{ kJ/mol}) \quad (2)$$
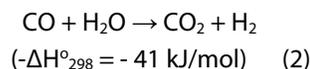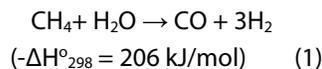
Decreasing the temperature to 600°C may reduce the energy consumption and the cost associated with the tubular reformer [2]. However, this decrease may affect conversion and catalyst activity. Utilizing the right support material may lead to better catalytic activities and resistance to coking even at relatively low operating temperature [3-5]. In our previous work, we investigated several support materials for nickel based catalysts, cerium as promoter and nickel optimum loading. Wherein, 15% and 20% of nickel and cerium loading respectively, on zirconia support gave better performance so far [4-8]. This study was focused on the comparison on the catalytic performance and characterization of $Ni/CeO_2/ZrO_2$ and commercial catalyst from Indonesia.

METHODOLOGY

The $Ni/CeO_2/ZrO_2$ catalyst was prepared using co-impregnation method. A 15% by weight (wt) and 20% wt of nickel and cerium respectively, were impregnated on zirconia oxide. The ZrO_2 (JRC-ZRO-4 reference catalyst) was provided by the Catalysis Society of Japan, while $Ni(NO_3)_2.6H_2O$ and $Ce(NO_3)_3.6H_2O$ precursors were from Sigma-Aldrich. The samples were dried at 40°C for 48 hours and then at 110°C for 24 hours. After drying, the samples were pulverized, then calcined at 600°C for 3 hours in the presence of air. The powder catalyst was pelletized, crushed and screened in order to collect uniform particles of 150-450 μm. The catalyst was then reduced using 20% hydrogen at 500°C for 1.5 hours.

The commercial catalyst that is being used in one of fertilizer industry in Indonesia as per December 2006 was investigated for the comparison. The 10 holed ring commercial catalyst was crushed and screened to get 150-450 μm mesh size particles as well.

The Autosorb Brunauer-Emmett-Teller (BET) analyzer from Quantachrome was used for surface-area measurement. The samples were degassed at 300°C for 1.5 hours for the gas removal before subjected to the measurement using nitrogen gas and helium as a carrier. The

Scanning Electron Microscope (SEM: JSM-5310LV Microanalyzer, JEOL Co.) and Energy Dispersive X-Ray Spectrometer (EDS: JED-2140 Microanalyzer, JEOL Co.) were employed to determine the surface morphology and the elemental identification respectively. The crystal structure was identified by Powder X-Ray Diffraction method (XRD: MultiFlex, Rigaku Co.). The actual loading of active material and the promoter was confirmed using SPS7800 Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES: Seiko). Hydrofluoric acid was used for the qualitative analysis of commercial catalyst, while in the quantitative analysis the prepared catalyst and the commercial catalyst were diluted in nitric acid solution and were evaluated with nickel nitrate and cerium nitrate standard solution. The basic sites of the catalysts were determined by Temperature Programmed Desorption (TPD) method using ammonia and carbon dioxide as its probe gases.

Catalytic activity experiments were carried out in a fixed bed micro-reactor at 600°C at atmospheric condition. One hundred mg of each sample was loaded into a six mm inside diameter of quartz micro-reactor with $H_2O/CH_4/He$ ratio of 3:1:6.7 at GHSV=96,000 h^{-1}. The H_2O was supplied using the micro-pump from Cole Parmer. Exit gases were analyzed in 30-minute intervals for 8 hours using a gas chromatograph (GC: GC-3200, GL-Sciences Co.). An ice bath was set up between the reactor exit and the sampling port in order to remove water from the effluent gas used for GC analysis. Methane conversion in steam reforming of methane was calculated as described below:

Methane conversion (%)
$$= \{(CH_{4in} - CH_{4out}) / CH_{4in}\} \times 100 \qquad (3)$$

The determination of total carbon deposits per gram of catalyst were conducted using Thermo plus thermogravimetric (TG: Thermo plus TG-8120, Rigaku Co.). About 20-30 mg of reacted catalysts were placed inside the apparatus using alumina pan. The samples were heated up to 900°C at the ramping rate of 10 K/min and hold for 30 minutes at 200, 600 and

900°C correspondingly. The helium was used as a carrier gas until 200°C only for the water and trapped gas removal purposes and followed by air as carrier for higher succeeding temperatures. An exothermic weight loss was observed at the temperature range between 600 and 900°C. This can be attributed to the combustion of deposited carbon. It is possible to estimate the amount of carbon deposition on the basis of this weight loss.

RESULTS AND DISCUSSION

Catalyst Characterization

Surface area measurement, elemental composition of the catalysts, crystal structure pattern and acid base measurement were conducted for the catalyst characterization.

Surface Characterization

Table I. Summary of Surface characterization using BET

Sample	Surface Area (m^2/g)	Pore Volume (cc/g)	Average Pore Size (Å)
Ni/CeO$_2$/ZrO$_2$	34.72	1.487 x 10^{-2}	1.362 x 10^2
Com – Cat	17.53	0.931 x 10^{-2}	1.390 x 10^2

High catalyst surface area is required since the reaction of the gases occurs at the surface of the active material. The BET results showed that the prepared catalyst has higher surface area than the commercial catalyst, this mainly due to the different support material of the catalysts which are zirconia and alumina that was confirmed from EDS, ICP and XRD results. Table I also shows that the pore volume of Ni/CeO$_2$/ZrO$_2$ catalyst also higher than the commercial catalyst although the average pore size has similar value at about 1.4x10^2 angstrom. The zirconia built uniform support for the active nickel on the

surface of the catalyst as can be seen at the image of SEM (Fig.1); the samples were pictured at 2000x magnification using SEM. Although Ni/CeO$_2$/ZrO$_2$ SEM image is denser than the commercial catalyst, the pore volume is even higher. This might be attributed to homogeneous pores in the catalyst and provide higher surface area as well.

(a) (b)
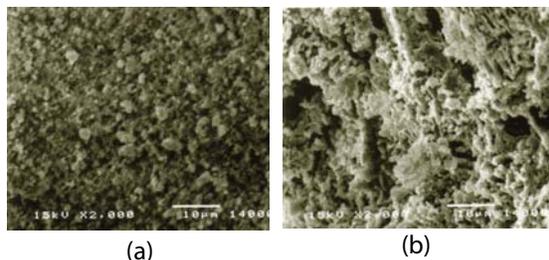
Figure1. SEM image of XRD pattern of Ni/CeO$_2$/ZrO$_2$ after reduction (a) and Commercial Catalyst (b)

Catalyst Composition

The EDS results from Table II show that the commercial catalyst is composed of various elements. The biggest portion was the aluminum and followed by nickel which was confirmed also in the ICP results. Hence, the commercial catalyst is a nickel based catalyst on alumina support. Other elements present in commercial catalyst might be the promoters that were used for improving the performance of the catalyst. In other hand, expected elements appeared in EDS for the prepared catalyst. The electron beam of EDS apparatus hits merely on the surface of the catalysts, hence the EDS results vary depending on the surface area struck by the electron beam. Table II also shows the ICP qualitative and quantitative results. The ICP quantitative results are reliable to determine the actual loading in the catalysts since the measurement based on the bulk catalysts that were digested in the solvent. Prepared catalyst has higher nickel loading than the commercial one. Desired weight of nickel and cerium loading at about 15% and 20 % respectively, were confirmed with the ICP results.

Table 2. Catalyst Element Composition And Actual Weight Loading

Sample	Element	EDS	ICP	
		% Atomic	Qualitative	% Weight Loading
Ni/CeO$_2$/ZrO$_2$	O	38.57	-	-
	Ni	16.73	-	14.55
	Zr	26.96	-	-
	Ce	17.74	-	19.44
Com - Cat	O	42.64	-	-
	Al	36.78	High	-
	Si	1.28	Low	-
	K	0.33	Low	-
	Ca	9.43	Low	-
	Ni	9.54	High	11.43
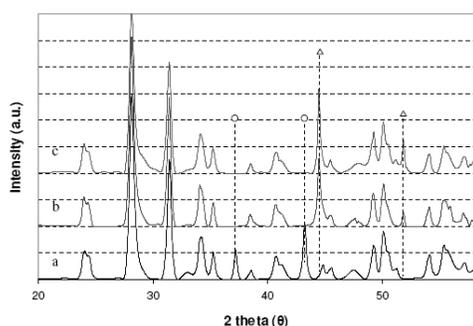
Figure 2. XRD Pattern of Ni/CeO$_2$/ZrO$_2$ Before Reduction (a), Ni/CeO$_2$/ZrO$_2$ After Reduction (b) and Ni/CeO$_2$/ZrO$_2$ After Reaction (c).
(o)NiO crystal; (Δ)Ni crystal

Figure 3. XRD pattern of Commercial catalyst Before Reaction (a) and Commercial Catalyst After Reaction (b).
(o)NiO crystal; (Δ)Ni crystal.

Crystal Structure of the Catalyst

The results of XRD pattern for the prepared and commercial catalysts are shown in Fig.2 and Fig.3 respectively. Based on the XRD library, the zirconia JRC-ZRO-4 has a crystal type of baddeleyite zirconia. In this paper, nickel crystal was expected in the prepared catalyst due to better reaction with CH$_4$ gas rather than nickel oxide. Peaks at 2 theta of 37.2, and 43.3, which correspond to the nickel oxide crystal, appeared on the prepared catalyst before reduction. After reduction, the mentioned peaks shifted to 2 theta of 44.5 and 51.8 which associated to the

nickel crystal. The XRD results after reaction also confirmed that the nickel crystal is stable during storage and even throughout the reaction without being oxidized in the present of air.

Fig.3 shows similar pattern with Fig.2 wherein nickel oxide crystals exist before the reaction and switched into nickel crystal peak after reaction. These results also give evidence that during the steam reforming reaction, the hydrogen product automatically will reduce

the catalyst from nickel oxide crystal into nickel crystal.

Acid-base Properties of the Catalyst

Based on the ammonia TPD pattern in Fig. 4, the calculation of acid sites per gram of commercial and prepared catalysts are 2.31×10^{19} and 3.37×10^{19} respectively. Meanwhile, from the carbon dioxide TPD pattern shown in Fig. 4 also, the basic sites per gram of commercial and prepared catalysts are 3.02×10^{19} and 4.89×10^{19} respectively. Both alumina and zirconia have amphoteric character; hence they have capability to behave as acid and base. However the prepared catalyst provide more acid sites which in SRM, the acidity of the catalyst will facilitate the decomposition of methane, but it might also promote cracking and polymerization, producing carbon. On the other hand, the prepared catalyst also provide more basic sites that enhance the activation of steam, dissociation into reactive OH and H species, lead to lowering the carbon formation. In addition, ceria also increase the basic sites because ceria itself is considered basic in nature; which may contribute in the carbon formation inhibition.

Catalytic Activity

Time-Course Methane Conversion

The catalytic activity was measured in terms of time-course percent (%) methane conversion. The time-course methane conversion at 600°C reaction operation temperature is presented in Fig. 5. At the first 10 minutes of reaction, the prepared catalyst has reached its maximum methane conversion at about 74.9% while the commercial catalyst still at 15.8% methane conversion. The lower conversion of commercial catalyst in the beginning reaction is owed to the changes of nickel oxide state onto nickel crystal by the hydrogen product. After all of the nickel oxide fully reduced into nickel crystal as an active site for the reaction to occur, then the commercial catalyst performed at 55.9% methane conversion after 30 minutes and above.

The difference on the catalytic activity could be influence from several factors. Different loading of the nickel as an active catalyst is one of its possibility. The surface area also contributes since it may increase the contact area for the reactions occur. Higher acid sites may also foster the decomposition of methane which promotes the reactions.

Figure 4. TPD pattern of NH₃ on Com-cat (a), CO₂ on Com-cat (b), NH₃ on Ni/CeO₂/ZrO₂ (c), CO₂ on Ni/CeO₂/ZrO₂ (d); and Temperature Profile (e)
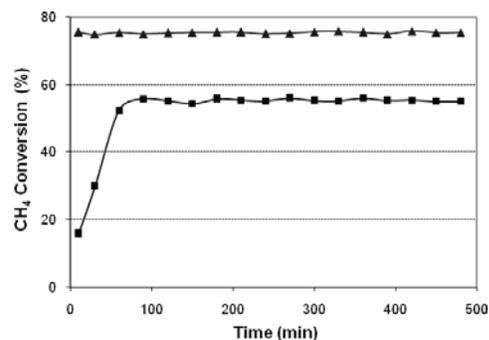
Figure 5. Time-Course Methane Conversion at 600 °C of Ni/Ce/ZrO₂ (▲) and Commercial Catalyts (■)

Effect of Temperature on Methane Conversion

Lowering the temperature at which the steam reforming reaction was conducted led to a decreasing percent (%) methane conversion as shown in Fig.6, where average percent methane conversion is plotted against reaction temperature. In general, both catalysts follow similar trend. However, at lower temperature than 600^oC, although required less energy consumption, the process it self could be not effective since big portion of methane will not be able to be converted to syngas.
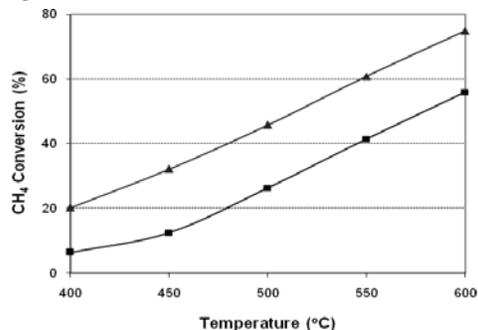
Figure 6. Average Methane Conversion at Various Steam Reforming Temperatures of Ni/CeO$_2$/ZrO$_2$ (▲) and Commercial Catalyst (■)

Coke Formation

The weight profiles using TG apparatus of 8 hours reacted catalysts at 600^oC operation temperature are shown at Fig.6. Different carrier gases were introduced in this experiment. Helium gas was used from room temperature until 200^oC in order to completely remove water content and trapped gases without interfering with the oxidation section when air was used as a carrier at temperatures greater than 200^oC. Both of the catalysts lost their moisture at similar % weight, and then oxidized by oxygen in the carrier starting from 200 to 600^oC. However, the nickel content in the prepared catalyst was higher than the commercial catalyst which led to the higher percent weight increase as the oxygen attached to the nickel crystal as shown in the TG result. The weight loss at higher TG

operation temperature from 600 to 900^oC was attributed to the carbon burning, which was deposited on the catalyst surface during the steam reforming of methane reaction.

The commercial catalyst weight loss was about 0.23% while in the prepared catalyst was 0.14% by weight. This could be attributed to the high oxygen storage capacity and to mobility of the oxygen atoms in the crystal lattice of cerium promoter combine with the amphoteric property of zirconia support in the prepared catalyst that increase the resistance toward coke formation.
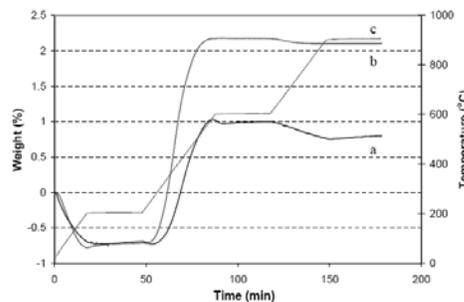
Figure 7. Weight Profile of Carbon Combustion using TG Commercial Catalyst (a), Ni/CeO$_2$/ZrO$_2$ (b), Temperature Profile (c)

Future Work

Insignificant deactivation that was observed in fig. 5 could not provide us with a sufficient data to calculate the lifetime of the catalyst. Although the carbon deposition of two third on the prepared catalyst was able to quantify, which give us approximation of 1.5 times longer than commercial catalyst in coking factor, but the deactivation of the catalyst could be also caused by other factors, such as sintering, poisoning or loss of active species. Hence; in the future it may be necessary to conduct an actual plant test or pilot plant using the prepared catalyst that will run for longer period, in example 6 or 12 months depending on the performance of the catalyst in order to review the catalyst before commercialization. On the other hand, the actual price comparison of prepared catalyst and commercial catalyst is one tenth. However,

this could not be used a basis price due to the difference in lab scale price (high purity and small quantity) compared with commercial product price. Once the prepared catalyst could be produced in large quantity, the lab scale price may also reduce.

CONCLUSIONS

The comparison of characteristics and catalytic activity of Ni/CeO$_2$/ZrO$_2$ prepared using the impregnation method and commercial catalysts have been investigated. The prepared catalyst has higher surface area at 34.72 m^2/gram and more uniform surface image compared to surface area of 17.53 m^2/gram of the commercial catalyst. The nickel weight loading of prepared catalyst was 14.55%, higher than the commercial catalyst at 11.43%. The catalyst was verified active in nickel crystal state and the nickel crystal was very stable during the storage and the reaction as well. More acid and basic sites were observed in the prepared catalyst at 3.37×10^{19} and 4.89×10^{19} per gram catalyst.

Higher methane conversion of 74.9% compare to 55.9% from commercial catalyst due to the higher nickel loading and better overall property of the prepared catalyst. More ever, after 8 hours catalytic reaction, the coke formation on the prepared catalyst reached 0.14% weight compared to 0.23% weight of the commercial catalyst. This coke resistant property of Ni/CeO$_2$/ZrO$_2$ catalyst could also prevent catalyst deactivation caused by carbon deposition which leads to longer catalyst life time.

ACKNOWLEDGMENT

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