Syngas Production via CO₂ Reforming of CH₄ over Zr-Ni/SBA-15

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Abstract. In the present study, the effect of Zirconium (Zr) promoter (1-7wt %) on the properties of Ni/SBA-15 for syngas from CO₂ reforming of CH₄ were studied. Zr-Ni/SBA-15 catalyst was prepared using a one-pot sol-gel method. The physiochemical properties of Zr-Ni/SBA-15 catalysts were characterized using XRD, BET and FTIR. Meanwhile the performances of the catalysts were tested using a stainless steel fixed bed reactor at 800 °C, atmospheric pressure and CO₂:CH₄ feed ratio of 1:1. The ordered mesoporous structure of SBA-15 support was proven by N₂ adsorption desorption isotherms. The surface area and pore volume of catalyst decreased with the increase of Zr loading as Zr and Ni particles occupied the SBA-15 frameworks and thus tended to expand the SBA-15 pore. ZrO₂ peak of 1Zr-Ni/SBA-15 was not detected in the XRD results indicating a good dispersion of the Zr species on the SBA-15 surface. The catalytic activity test revealed that the optimum Zr loading was 1 wt% with CH₄ conversion, CO₂ conversion and H₂:CO ratios of 87.07%, 74.01%, and 0.42 respectively. This was due to the presence of the Zr species that promoted a better dispersion of Nickel (Ni) active sites on the SBA-15 surfaces as proven by the XRD and FTIR analysis. All catalysts maintained good catalytic activity up to 900 °C with less than 5 % weight loss as analyzed by TGA.

1. Introduction
In recent years, considerable attention has been paid on the global warming issue due to the negative effects of greenhouse emissions into atmosphere to human health and the environment. Studies on the CO₂ reforming of CH₄ have gained significant research interest recently as this route can convert greenhouse gases (CO₂ and CH₄) into valuable syngas. The consumption of two major greenhouse gases (CO₂ and CH₄) by dry methane reforming and their conversion to syngas gives to this process a great interest for the purposes of environmental protection and natural gas vaporization [1]. CO₂ reforming of CH₄ is a process where methane reacts with carbon dioxide over a catalyst which produces syngas typically in an equal H₂/CO ratio which is appropriate for the production of Fischer–Tropsch liquid hydrocarbon and oxygenates. The advantages of this process are mitigation of CO₂ and natural gas emission into the atmosphere, transformation of natural gas and CO₂ into valuable syngas and effective utilization of low-grade natural resources consisting of natural gas and CO₂. Therefore, the carbon dioxide reforming of methane is a good route for producing high added value fuels such as hydrogen.
A lot of studies on the CO$_2$ reforming of CH$_4$ have shown that Ni-based catalysts were the most efficient for the production of H$_2$ and syngas comparable in some studies to noble metals (Ru, Rh and Pt) [2][3]. The performances of Ni-based catalyst depend on many factors including type of support materials, Ni active sites, Ni dispersion, and preparation method of catalyst. However, the Ni based catalysts tend to form coke and deactivate easily due to the Ni sintering [4][5]. Inhibition of Ni sintering can be done by controlling the metal size and enhancing the metal dispersion. The stabilization of the Ni particles against thermal sintering is achieved due to the strong metal-support interaction through the addition of secondary metal oxides as promoters to the support.

Several metal oxides which commonly act as promoters such as CaO [6] MgO [6][7], CuO [8][9], CeO$_2$ [10][11][12], La$_2$O$_3$ [13] and ZrO$_2$ [18] have been frequently introduced as promoters to stabilize the Ni particles on the support. The addition of promoters such as ZrO$_2$ and CeO$_2$ to Ni/SBA-15 catalyst tends to improve the oxygen storage capacity which then enables the absorption and release of O$_2$ during oxidizing and reducing conduction which in turn acts as a strong inhibitor for coke formation during reaction. Among these promoters, ZrO$_2$ is a promising candidate due to its high thermal stability in both oxidizing and reducing atmospheres. Moreover, ZrO$_2$ promotes the gasification of adsorbed intermediates, which are precursors for carbon formation and responsible for the main deactivation mechanism in CO$_2$ reforming of CH$_4$. However, high amount of ZrO$_2$ loading could greatly reduce the surface area of the support leading to low dispersion of nickel particles. Therefore, it is important to know the ideal amount of Zr loading which can greatly reduce the coke formation while maintaining a high rate of reaction.

In the present study, the amount of Zr loaded onto Ni/SBA-15 via sol gel method was studied, in order to determine the influence and limitation of Zr promoter on Ni/SBA-15 catalyst towards CO$_2$ reforming of CH$_4$.

2. Experimental

2.1. Catalyst preparation

Zr/Ni-SBA-15 catalyst was prepared by the sol-gel method as described in an earlier publication [2]. Specifically, triblock copolymer Pluronic P123 (EO$_{20}$PO$_{70}$EO$_{20}$) was used as the structure directing agent and Tetraethylorthosilicate (TEOS) as the silica support source for the catalyst. An adequate amount of P123 was dispersed in TEOS under vigorous stirring at 60 °C for 10 minutes to obtain a homogeneous solution. The ethanol solution containing a requisite amount metal precursor solutions, Ni(NO$_3$)$_2$ and Zr(NO$_3$)$_4$ corresponding to different Zr to Ni/SBA-15 molar ratio was added to the above solution under constant stirring at 60 °C for another 10 minutes. After the solution cooled down to room temperature, 2.0 ml of hydrochloric acid was added to the mixture under constant stirring for 2 hours. After being stored at room temperature for 24 hours, a light green gel formed, and it was transferred into an oven at 110 °C and the drying process continued for 4 hours. Finally, the pre-dried sample was calcined in a muffle furnace at 800 °C for 5 h in air, yielding the Zr-Ni/SBA-15 catalyst. For all catalysts produced, the Ni content was fixed at 5 wt% and the Zr content was varied from 1 wt% to 7 wt%.

The products denoted as x-Zr-Ni/SBA-15, where “x” indicates the molar ratio of Zr to Ni/SBA-15.

2.2. Catalyst characterization

The crystalline structure of the catalysts was characterized by X-ray diffraction (XRD) recorded on a (Rigaku Miniflex II, 45 kV, 40 mA) powder diffractometer using a Cu Kα radiation ($\lambda = 1.5405\text{Å}$) with scanning temperature from 10 °C (283K) to 80 °C (353K) at 4 min$^{-1}$. The average NiO and ZiO crystal size were determined by using the Scherrer equation:

$$D = \frac{0.9\lambda}{\beta \sin \theta}$$  

(1)
where \( \lambda \) is the X-ray wavelength corresponding to Cu-K\( \alpha \) radiation (0.15405 nm), \( \beta \) is the broadening (in radians) of the nickel (200) reflection and \( \theta \) is the angle of diffraction corresponding to peak broadening.

The Brunauer–Emmett–Teller (BET) surface areas of the Ni catalysts were determined in AUTOSORB-I model AS1 MP-LP analyzer. Prior to the BET analysis, the samples were degassed at a temperature of 120 °C for 12 h before being subjected to N\(_2\) adsorption. The chemical properties and the interaction of Ni with SBA-15 support were analyzed by the Fourier Transform Infrared (FTIR), recorded using LTI’s fully-computerized Fourier Transform Infrared Spectroscopy system which generates the absorbance spectra showing the unique chemical bonds and the molecular structure of the sample material. Thermogravimetric analysis (TGA) of the sample was carried out in Q500-series model TGA unit under the mixture of air (20% O\(_2\)/80% N\(_2\)) with heating rate of 10 °C min\(^{-1}\) up to 900 °C to measure the amount of weight loss during CO\(_2\) reforming of CH\(_4\) reaction.

2.3. Catalytic testing
The catalytic activity of the catalysts for CO\(_2\) reforming of CH\(_4\) was conducted in a stainless fixed bed reactor (i.d. 11 mm, length 417 mm) under atmospheric pressure at 800 °C as shown in Figure 1. A thermocouple was placed in the tube with one end touching the catalyst in order to monitor the bed temperature inside the reactor. Prior to the reaction, 0.2 g of catalyst was placed between two layers of quartz wool before being reduced in 50 ml/min of H\(_2\) flow at 700 °C for 1 h. A mixture of CH\(_4\):CO\(_2\):N\(_2\) with ratio 1:1:1 and total flow rate 50 ml/min was fed into the reactor. The reaction was run at 800 °C for 5 h. The effluent gas was analyzed with an Agilent gas chromatograph (AGILENT 6890 N) equipped with a thermal conductivity detector (TCD). The conversion of CH\(_4\) and CO\(_2\), and ratio of H\(_2\)/CO were defined as follows:

\[
\text{CO}_2 \text{ Conversion, } X_{\text{CO}_2} (\%) = \frac{F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}}}{F_{\text{CO}_2,\text{in}}} \times 100\%
\]  

(2)

\[
\text{CH}_4 \text{ Conversion, } X_{\text{CH}_4} (\%) = \frac{F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}}{F_{\text{CH}_4,\text{in}}} \times 100\%
\]  

(3)

\[
\frac{\text{H}_2}{\text{CO}} = \frac{F_{\text{H}_2}}{F_{\text{CO}}}
\]  

(4)

where \( F \) is the molar flow rate for particular compound.
3. Results and Discussion

Figure 2 shows the complete XRD patterns of the catalyst samples, the broad diffraction peaks at 2θ = 23° indicates the amorphous nature of SBA-15 which is consistent with literature [14]. The sharp diffraction peaks for NiO species were observed for all the calcined samples at 2θ = 37.2°, 43.1°, 62.8° and 75.4°, corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) of cubic NiO species. As seen in Figure 2, the peak intensities of NiO were increased with the Zr loading which suggested a more crystalline phase of NiO on the SBA-15 surfaces. Interestingly, NiO diffraction peaks of the 1Zr-Ni/SBA-15 catalyst shifted to a higher angle, which indirectly reflects to the presence of the small NiO particles on the SBA-15 support. The characteristic peaks at 2θ = 28.2° and 31.5° were attributed to the ZrO2 [15]. The ZrO2 peak was more intense with the increasing of Zr loading from 3 to 7 wt%. However the ZrO2 peaks were not detected for 1Zr-Ni/SBA-15 catalyst due to the complete incorporation of Zr species into the SBA-15 pores.

Figure 1. Process Flow Diagram of the CO₂ Reforming of CH₄. (1) Regulator, (2) Valve, (3) Mass Flow Controller, (4) Gas Chamber, (5) Vertical Tube Furnace, (6) Temperature Controller, (7) Condenser
The physiochemical properties of Zr-Ni/SBA-15 catalyst obtained from N\textsubscript{2} adsorption desorption isotherms are tabulated in Table 1. The BET surface area and total pore volume of the catalysts decreased from 240 to 170 m\textsuperscript{2}/g and 0.411 to 0.368 cm\textsuperscript{3}/g, respectively after the Zr introduction from 1-7 wt%. Further increase in the amount of Zr loading on to the SBA-15 support resulted in significant reduction of the pore volume and increase in the pore diameter. This phenomenon indicates that most of the SBA-15 pores are occupied by Ni and Zr particles which then caused the expansion of SBA-15 pore diameter as well as pore mouth blockage. Similar trends were reported in literature upon addition of Ce to Ni/SBA-15 [2]. In contrast, the pore diameter of the catalyst increased as the Zr loading increased from 1-7 wt% possibly due to the expansion of SBA-15 pores by the incorporation of Zr with the SBA-15.

![Figure 2. Wide angle of XRD pattern of a) 1Zr-Ni/SBA-15, b) 3Zr-Ni/SBA-15, c) 5Zr-Ni/SBA-15 and d) 7Zr-Ni/SBA-15](image)

| Catalysts      | BET Surface Area (m\textsuperscript{2}/g) | Pore Volume (cm\textsuperscript{3}/g) | Pore diameter (nm) | NiO particle size\textsuperscript{a} (nm) | ZrO particle size\textsuperscript{a} (nm) |
|----------------|----------------------------------------|-----------------------------------|--------------------|----------------------------------|----------------------------------|
| 1ZrNi/SBA-15  | 240                                    | 0.411                             | 6.1                | 20.9                             | -                                |
| 3ZrNi/SBA-15  | 216                                    | 0.378                             | 6.2                | 34.7                             | 22.0                             |
| 5ZrNi/SBA-15  | 199                                    | 0.393                             | 6.2                | 37.8                             | 19.5                             |
| 7ZrNi/SBA-15  | 170                                    | 0.368                             | 6.3                | 36.7                             | 19.4                             |

The N\textsubscript{2} adsorption and desorption of Zr-Ni/SBA-15 catalysts are presented in Figure 3. All samples showed H4 type hysteresis at the P/P\textsubscript{0} range of 0.4 to 0.75. The gas uptake at the range P/P\textsubscript{0} 0.4 to 0.8 corresponded to the adsorption in the mesopores and on the external surface [16] and the gas uptake that occurred between 0.8-1.0 was typical for micropores. This result indicates the presence of micropores and mesopores in all samples due to the structural degradation of the hexagonal structure of SBA-15 when Zr was added.
The FTIR spectra of SBA-15 and Ni/SBA-15 in the range 500-1400 cm\(^{-1}\) and 2500-400 cm\(^{-1}\) were shown in Figure 4. Based on the result in Figure 4 (A), the band detected at 960 cm\(^{-1}\) is credited to the Si-OH non-bridging oxygen stretching vibration. A slight decrease of the band vibration is noticed with increasing of Zr loading, which could be related to the substitution of hydrogen atoms in O-H bonds with O-Zr to form Si-O-Zr. The absorption peaks at 1060 cm\(^{-1}\) and 801 cm\(^{-1}\) were assigned to Si–O–Si asymmetric stretching and symmetric stretching of the SBA-15 framework, respectively. In addition, the observed peak at 3689cm\(^{-1}\) in Figure 4 (B), assigning to the Si-OH stretching vibration of O–H in adsorbed H\(_2\)O molecules was decreased with the increase of Zr loading. The band changes were due to the replacement of O-H bonds in water molecules with O-Zr when the Zr was introduced. It can be concluded that band changes at 960 and 3689 cm\(^{-1}\) could prove that metal was incorporated into the framework of the tetrahedral silica.
4. Catalytic testing

Figure 5 presents the effect of Zr loading on CO\textsubscript{2} reforming of CH\textsubscript{4}. As observed, the conversion of CH\textsubscript{4} was slightly higher than CO\textsubscript{2} over all Zr-Ni/SBA-15 catalysts except 7Zr-Ni/SBA-15. This was owing to the occurrence of CH\textsubscript{4} cracking along the reaction process, as it was favourable at reaction temperatures exceeding 600 °C [2]. The average conversion CO\textsubscript{2} and CH\textsubscript{4} was found to decrease from 1 wt% of Zr to 7 wt% of Zr at 800 °C. For the catalyst sample with 1 wt% of Zr the conversion was considerably higher compared to other catalysts at 87.27 % and 74.01 % for CH\textsubscript{4} and CO\textsubscript{2} respectively with a H\textsubscript{2}/CO ratio of 0.42. It appears that increasing the Zirconium content loaded onto Ni/SBA-15 would decrease the conversions by more than half with CO\textsubscript{2} conversion dropping from 74.01% to 32% and CH\textsubscript{4} dropping from 87.27% to 34% at 7 wt% Zr. Furthermore, a deterioration of CH\textsubscript{4} conversion for the first 30 minutes of reaction was observed over 3Zr-Ni/SBA-15. This was probably due to the destabilization of ZrO\textsubscript{2} interaction with the Ni and SBA-15 support as the particles became larger compared to other catalysts (see Table 1). For the catalyst with 5 wt% and 7 wt%, the conversion of CO\textsubscript{2} and CH\textsubscript{4} were lower than 45%. This might be due to the increase in Zirconium species embedded into the SBA-15 mesoporous structure instead of Nickel. The overload of Zirconium would reduce the dispersion of the Nickel which tended to agglomerate and block the pores of the SBA-15. This aggravates the sintering effect of the Nickel species at the high reaction temperature of 800 °C. Consequently, the active sites of Nickel particles aggregated during the reaction and catalyst sintering occurred which may be one cause for the catalyst deactivation. As a result, the catalytic performance of catalyst samples with 3 wt%, 5 wt% and 7 wt% Zirconium promoter dropped dramatically. For the catalyst sample with 1 wt% of promoter, Zirconium is well dispersed and promotes the Nickel species to be confined to the pores of SBA-15 as proven by XRD and FTIR analysis. Thus, the Nickel species does not undergo sintering as it is well embedded in SBA-15 and subsequently can withstand higher temperatures [17].

The Zr species enhanced the dispersion of the Ni species on the Zr-Ni/SBA-15 catalyst's surface. The introduction of promoter Zr changed the nature of the active center, promoting the formation of active sites for the target reaction. Zr promoted catalysts facilitated the activation of C–H bond in CH\textsubscript{4}. Besides,
different relative proportions of carbonates were formed from CO$_2$ which affected the activation of CO$_2$. This indicates that Zr-Ni/SBA-15 catalysts facilitated the activation of CO$_2$. Moreover, the introduction of Zr promoter led to the quicker formation and decomposition of intermediate formats [17].

Figure 5. A) CH$_4$ conversion and (B) CO$_2$ conversion of Zr-Ni/SBA-15 catalysts in CO$_2$ reforming of CH$_4$. (C) Effect of different nickel loading on the CH$_4$ conversion, CO$_2$ conversion, and H$_2$/CO ratio.
5. Catalyst deactivation

Figure 6 showed the TGA analysis of the spent 1Zr-Ni/SBA-15, 3Zr-Ni/SBA-15, 5Zr-Ni/SBA-15 and 7Zr-Ni/SBA-15. The initial weight loss was observed for Zr-Ni/SBA-15 catalysts from 80 to 250 °C which was attributed to loss of water content. It is observed that the weight loss of 1Zr-Ni/SBA-15 was lower than that of the other three catalysts which might be due to the reduction of hydrogen interaction between silanols and absorbed water by substitution of O-H with O-Zr. The slight increase of the curve around 600°C was due to the oxidation of deposited carbon; while the weight loss that occurred between 700 °C to 900 °C was due to the oxidation of inert graphite carbon that is responsible for deactivation of Zr-Ni/SBA-15 catalysts. The TGA analysis obviously showed that 1Zr-Ni/SBA-15 had the lowest coke deposition due to higher amount of Si-O-Ni interaction that enhance its catalytic performance during CO₂ reforming of CH₄.

![TGA analysis for spent catalyst](image)

**Figure 6.** TGA analysis for spent catalyst

6. Conclusion

Different Zr loading of Zr-Ni/SBA-15 catalysts prepared by sol-gel method were well preserved in the mesoporous structure of SBA-15 as proven by BET analysis. 1Zr-Ni/SBA-15 showed the high catalytic activity with CH₄ conversion, CO₂ conversion and H₂/CO ratio of 87.07%, 74.01%, and 0.42, respectively. This result showed the positive effect of Zr on enhancement of Ni active sites dispersion on the SBA-15. This would create a good metal-support interaction that then favours the reaction of CO₂ reforming of CH₄ with high stability of the catalyst.

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