Syngas production via dry reforming of methane over Ni-based catalysts

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Abstract. Dry reforming of methane (DRM) is emerging as an enticing research area due to the crucial requirement to mitigate global environmental issues and offers as an alternative energy resource. However, the DRM commercialized prospect and industrial utilization are curbed due to the weak prospect of sustained activity of the catalysts. The objective of this research is to find out the effects of the addition of CeO$_2$ and La$_2$O$_3$ as promoters on the performance of the catalyst. In this work, catalysts such as Ni/Al$_2$O$_3$, Ni/Al$_2$O$_3$-CeO$_2$, Ni/Al$_2$O$_3$-La$_2$O$_3$ were prepared by sol-gel method. The prepared catalysts have been characterized by XRD, BET analysis, and temperature-programmed reduction (TPR). BET results revealed that the addition of CeO$_2$ and La$_2$O$_3$ slightly decreased the BET surface area of the synthesized catalyst because of the deposition on the porous structure of the support and filling its pores. The performance of the catalysts in DRM at 800°C shows that catalyst with CeO$_2$ have the highest and stable conversion, while La$_2$O$_3$ has a significant role towards the stability of the reaction during the 8 h reaction on stream.

1. Introduction

Fossils fuels such as oil, coal and natural gas currently provide a large proportion of the global energy requirements. Energy generation from these fuels and their processing contribute to significant emissions of greenhouse gases (GHG), i.e. carbon dioxide (CO$_2$) and methane (CH$_4$), which contribute to global warming issues and associated environmental changes [1, 2]. Several efforts attempt to limit...
CO₂ and CH₄ emissions in order to minimize environmental issues. One significant possibility to overcome the environmental issue is the application of conversion of methane into a synthesis gas also known as syngas (a mixture of H₂ and CO) which can be further processed to produce fuels and chemicals [3-7]. Synthesis gas can be produced from coal, biomass, petroleum coke, and natural gas [8, 9]. However, the cheapest and most environmentally friendly methods until the date of production of syngas are based on natural gas [7].

The catalytic steam reforming of methane (SRM) reaction is the prevalent and conventional route to produce syngas [10, 11]. Due to the high H₂: CO ratio of higher than 3 and a large amount of undesired CO₂ produced are always the main setbacks encountered with this approach. Also, SRM is an exorbitant process and requires intensive energy input due to its endothermic nature [11]. In addition, DRM utilizes two greenhouse gases, i.e. CO₂ and CH₄, to produce syngas. The advantage of the application of DRM for syngas production lies ideally in the same molar ratio of H₂ and CO, i.e. unity, which provides an appropriate formation of oxygenated compounds towards synthetic fuels by employing the Fischer-Tropsch process [12, 13].

The application of a catalyst is vital during the reforming of methane for complete conversion of the reactants. Although Ni-based catalysts have been widely used in industrial practices and research because they are easily available, highly active, affordable and morphological [20-21]. However, it has been extensively reported that they prone to carbon deposition that causes the deactivation of catalysts, leading to acute operational problems in industrial processes [12-14, 16]. A lot of effort has been put into the design and synthesis of stable Ni catalyst with high carbon resistance. Addition of La₂O₃ in Ni-Al catalyst can be beneficial by inhibiting coke formation during the reaction of dry reforming of methane and reduce the acidity of the support, this favors the chemisorption and dissociation of carbon dioxide and thus eliminates carbon by reverse Boudouard reaction [17].

Furthermore, the dispersion of La₂O₃ over Al₂O₃ and Ni crystallites prevents the growth of Ni grains at high temperatures, which result in reducing the sintering of catalyst due to the formation of La₂O₃CO₃ [18]. On the other hand, ceria has a characteristic of releasing and storing oxygen. As a result reduction of Ce⁴⁺ to Ce³⁺, which leads to the formation of oxygen vacancies. Therefore, finding a new catalyst that can resist to deposition of carbon through the use of suitable support and promoter is vital in DRM.

In the present study, we report a comparison involving the effect of Ce and La promoters on the physio-chemical properties of Ni/Al₂O₃ catalysts, synthesized by sol-gel method. The catalysts were characterized to describe the effect of promoters, i.e. Ce and La on the catalyst performance.

2. Materials and Methods

2.1. Catalyst Preparation
The catalysts Ni/Al₂O₃ (CAT-1), Ni/Al₂O₃-CeO₂ (CAT 2), and Ni/Al₂O₃-La₂O₃ (CAT 3) were synthesized by sol-gel technique [19]. The preparation has started by mixing stoichiometric amounts of Ni(NO₃)₂.6H₂O, (Al₂O₃)₉.9H₂O, either Ce(NO₃)₃.6H₂O or La(NO₃)₃.6H₂O and citric acid as a chelating agent were dissolved in deionized water. The solution has then been heated on the hot plate up to 80°C and has been stirred for 8h continuously until the gel is formed. The gel has been placed in an oven at 393K for a duration of 10+ hours before it has been calcined 1173.15 K for 5h. The nickel-metal loading was 10 wt%, and the CeO₂ and La₂O₃ promoters were 10%.

2.2. Catalyst Characterization
X-Ray Diffraction (XRD) technique has been utilized to characterize the calcined mixed oxide catalysts by employing Bruker D8B Advance X-ray diffractometer within the angle range of $2\theta$ =10–90°. The existing phases present in the samples have been identified by comparing them with reference samples held in the database by International Centre for Diffraction Data (ICDD). Temperature Programmed Reduction (H2-TPR) analysis have been performed using Thermo Scientific 1100. In this study, 50 mg of the catalyst has been heated in a reactor at 250°C for 1 hour in the presence of N2, flow of 20 mL min$^{-1}$. The catalyst samples were degassed by injecting hydrogen flow; after this, the catalyst is heated from 40 to 1000°C. For basicity calculation, the materials were first pretreated at 500°C for 1 h, then cooled to 80°C. BET Surface Area Analysis (BET) analysis using Micromeritics ASAP 2020 to measure the surface area of catalytic materials by N2 adsorption using BET isotherm.

2.3. Catalyst Evaluation
The DRM reaction was carried out in a tubular furnace reactor. Typically, 0.2 g of catalyst sample with the help of quartz wool was placed in the center of the stainless tube of the reactor. Agilent 7820A series gas chromatography was used to evaluate the post-reaction gases.

3. Results and Discussion

3.1. BET Surface Area Analysis
Table 1 tabulates the textural properties, i.e. surface area, pore size and pore volume for the three catalysts. The surface area measured by the BET method is the highest for CAT-1, the catalyst without any promoter. The higher value showed by the catalyst is due to the alumina trait. It presents an area of 138.1 cm$^2$/g. The table also shows the decrease of BET surface area when CeO$_2$ and La$_2$O$_3$ promotors are introduced, with 126.9 cm$^2$/g and 125.0 cm$^2$/g values, respectively. The decreases in BET surface area probably due to the CeO$_2$ and La$_2$O$_3$ coverage of alumina pores [20]. Also, it is possible to note that there is a slight difference in the values between the addition of the two promotors. The average pore size and pore volume followed the same trend as BET; CAT-1 has the 6.3 nm and 0.3 cm$^3$/g values of pore size and pore volume, respectively. However, these values decrease with the addition of CeO$_2$ and La$_2$O$_3$ promotors because of the blockages of the pores.

| Catalyst | BET Surface Area (m$^2$/g) | Pore Size (nm) | Pore Volume (cm$^3$/g) | Average Crystal size$^a$ (nm) |
|----------|-----------------------------|----------------|------------------------|-------------------------------|
| CAT-1    | 138.1                       | 6.3            | 0.30                   | 4.1                           |
| CAT-2    | 126.9                       | 5.6            | 0.25                   | 2.7                           |
| CAT-3    | 125.0                       | 5.5            | 0.24                   | 20.1                          |

$^a$ Determined by the Debye–Scherrer equation of the NiAl$_2$O$_5$ peaks of XRD.

3.2. XRD Analysis
The patterns of catalysts CAT 1, CAT 2 and CAT 3 are recorded within the scan range of 10-90° and step size of 0.04°/step. Figure 1 shows the XRD pattern of fresh Ni/Al$_2$O$_3$ catalysts with their respective combine of the promoter. The result of XRD shows the presence of Al$_2$O$_3$, NiAl$_2$O$_4$ and CeO$_2$ crystalline phases. Ni or NiO crystalline peaks do not appear on the graph, which indicates that Ni particles are small and highly dispersed on the surface of the support [21]. Diffraction peaks of alumina, Al$_2$O$_3$ (JCPDS 00-010-0339) appear at (2θ= 37.2°, 45.4°, and 66.4°) at the index of (311), (400), and (440), respectively. The NiAl$_2$O$_5$ spinal peaks can be seen, but the peaks overlap of that of alumina as has been a report in a previous study [21]. The coexistence of both Al$_2$O$_3$ and NiAl$_2$O$_4$ phases indicates that 10 wt.% Ni is not enough to transfer all gamma phase of Alumina into NiAl$_2$O$_4$ [22].
CAT-2 containing CeO$_2$ shows peaks at 2$\theta$ of 28.7°, 33.3°, 47.6° and 56.5° (JCPDS 00-004-0593) which represent the fluorite structure of ceria. On the other hand, the diffractogram of CAT-3 containing La$_2$O$_3$ has the least structure crystallinity reveals that La$_2$O$_3$ is amorphous and has a small reflection at the same peaks as that of Al$_2$O$_3$. The average crystal sizes of the catalysts are calculated using the Debye–Scherrer equation and presented in table 1.

3.3. $H_2$-TPR Analysis

Figure 32 displays the TPR analysis for the three catalysts. The TPR patterns of the catalysts are below 850°C which indicates that NiO was reduced to metallic Ni with obvious differences among the peaks. Both promoted catalysts show higher peaks of hydrogen consumption compared to Ni/Al$_2$O$_3$. CeO$_2$ and La$_2$O$_3$ are structural promoters that can limit the aggregation of Ni particles during the reduction of H$_2$ [23]. The peaks at low temperatures, about 300-450 °C, can be attributed to the reduction of Ni that weakly interacts with the support. CAT-1 shows a small shoulder of these species and more pronounced peak for that of CAT-2 and CAT-3, which indicate that CeO$_2$ and La$_2$O$_3$ promoters improve the reduction of Ni. CAT-2 shows the largest reduction peak for NiO around 400°C, implying that the presence of CeO$_2$ facilitates the dispersion of large fraction of NiO species and that are weakly attached to the support. Figure 4 also shows the second peak at 500°C for CAT-1 and CAT-2 and 550 for CAT-3. This peak is ascribed to the reduction of Ni that is moderately attached to the support. The reduction peak observed around 800°C for CAT-1 corresponds to the formation of Nickle aluminate, which evidences the formation of the strong interaction between Ni and the support [20].
3.4. Reaction Test Performance

The activity of catalyst controls the extent of a chemical reaction and determines the effectiveness of catalyst towards the rate of chemical reaction and conversion of reactants. The dry reforming reaction at 800°C for 8h is presented in figure 3. Fig. 3(a) compares the CH₄ conversion and can be seen that CeO₂ and La₂O₃ have a perceptible influence on catalytic performance. CAT-1 and CAT-3 show the same initial conversion of 73%. Al-Fatesh et al. [17] showed that La₂O₃ as promotor plays a dual role in dry reforming reaction; it prevents the disposition of carbon during the reaction and decreases the acidity of the support. Hence it stops the pyrolytic carbon formation and favors the dissociation of CO₂. On the other hand, CAT-2 has the highest conversion with 88% initial conversion. Besides, the catalyst demonstrates prominent stability over the hrs on stream. This can be associated with catalyst properties evidenced by H₂-TPR Fig. (2). It is known that CeO₂ promotion allows better dispersion of the active spices on the catalyst surface compared to the mono-oxides or bare support, without the addition of promoter [13]. The coexistence of CeO₂ with other oxides increases the reducibility and the oxygen storage capacity of the catalyst [24]. Damyanova et al. [25] have shown that a small amount of CeO₂, say 6 wt% can stabilize the textural properties of modified ZrO₂ with CeO₂.

In the same manner, CO₂ conversion as shown in figure 3(b) is in the same trend as that of CH₄ conversion. CAT-1 and CAT-3 have the same initial conversion of 83%. CAT-3 maintain stable conversion compared to CAT-1. CAT-2 demonstrates the best conversion and stability. However, conversion of CO₂ is higher than CH₄ conversion because of the simultaneous generation of reverse water gas shift (RWGS) reaction [26]. The RWGS reaction involves the reaction of CO₂ with H₂ to form CO. This result is also reflected in the molar ratio of H₂/CO, where the ratio is always lower than 1 as shown in figure 3(c). In general, the H₂/CO ratio is around 0.89, 0.94 and 0.87 for CAT-1, CAT-2, and CAT-3, respectively.
Figure 3. Catalytic performance of the synthesized catalysts, (a) CH$_4$ conversion, (b) CO$_2$ conversion and (c) H$_2$/CO ratio at 800°C; feed ratio CH$_4$:CO$_2$:N$_2$ = 1:1:1; and feed flow rate=60 mL/min.

4. Conclusion
A comparison of three synthesize catalysts which are CAT-1, CAT-2 and CAT-3 were made. The addition of CeO$_2$ as combined support with Al$_2$O$_3$ has improved the dispersion, increases the active metal content on the catalyst surface, enhanced the reducibility and the catalyst basicity. This has reflected on the performance of the catalysts, where the higher and stable conversion was achieved. On the other side, the addition of La$_2$O$_3$ did not increase the conversion of the reactant, but it maintained relatively stable conversion over the 8 hours on stream. This is because La$_2$O$_3$ contributed to the removal of deposited carbon during the reaction.

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