The Ni Catalyst Supported on the FSP-made Transition Metal (Co, Mn, Cu or Zn) Doped La$_2$O$_3$ Material for the Dry Reforming of Methane

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Abstract

The transition metal (Co, Mn, Cu or Zn) doped La$_2$O$_3$ material was prepared by flame spray pyrolysis (FSP) technique. The 2 wt.% Ni catalyst supported on this material was characterized by XRD, N$_2$ physisorption, TPR, H$_2$ chemisorption and TGA, and evaluated by the dry reforming of methane (DRM). The perovskite structure was certainly formed when either Co or Mn was introduced. The Cu can generate the La$_2$CuO$_4$ spinel phase while the Zn showed a mixed phase of La$_2$O$_3$, ZnO and La(OH)$_3$. The Ni/Co-La$_2$O$_3$ catalyst was more active for the DRM because of high amount of active dual sites of Ni and Co metals dispersed on the catalyst surface. The formation of La$_2$O$_2$CO$_3$ during the reaction can inhibit the coke formation. The cooperation of La$_2$O$_2$CO$_3$ and MnO phases in the Ni/Mn-La$_2$O$_3$ catalyst was promotional effect to decrease carbon deposits on the catalyst surface. The partial substitution of Co for Mn with a small content of Mn can enhance the catalytic activity and the product yield. The Ni/Mn$_{0.05}$Co$_{0.95}$-La$_2$O$_3$ catalyst showed the highest CH$_4$ conversion, H$_2$ yield and H$_2$/CO ratio. The Mn inserted into the perovskite structure of LaCoO$_3$ was an important player to change oxygen mobility within the crystal lattice to maintain a high performance of the catalyst.

Keywords: Ni/Co-La$_2$O$_3$; Ni/Mn-La$_2$O$_3$ Flame spray pyrolysis; Perovskite; Dry reforming of methane

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1. Introduction

It is well-known that global warming is caused by emission of greenhouse gases including carbon dioxide carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxides (N$_2$O), chloro-fluorocarbon (CFC) and ozone (O$_3$). The CO$_2$ and CH$_4$ have cause the global temperature to raise, polar ice to melt, loss of balance to the ecosystem and natural disasters [1–3]. The CO$_2$ reforming of CH$_4$ or the dry reforming of methane (DRM) reaction attracts interest for converting CO$_2$ and CH$_4$ to the syngas (CO and H$_2$). The DRM not only helps in decreasing toxic airborne emissions but also allows production of the syngas with a H$_2$/CO ratio equal to unity. This syngas is the starting feedstock of methanol synthesis and Fischer-Tropsch synthesis (FTS) [4]. The main reaction of the DRM is expressed in Equation (1). In general, this reaction is able of promoting other undesired reactions, which are the reverse water gas shift reaction, the methane decomposition, and the Boudouard’s reaction as shown in the Equations (2)-(4), respectively [5,6]. The DRM is highly endothermic reaction

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and requires high temperatures to obtain high conversions of methane [7]. As a consequence, the major problem is catalyst deactivation due to the accumulation of carbon on the catalyst surface and sintering at high temperature [8,9].

\[
\begin{align*}
\text{CH}_4 + \text{CO}_2 & \leftrightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H = 247 \text{ kJ.mol}^{-1} \quad (1) \\
\text{CO}_2 + \text{H}_2 & \leftrightarrow \text{H}_2\text{O} + \text{CO} \quad \Delta H = 41 \text{ kJ.mol}^{-1} \quad (2) \\
\text{CH}_4 & \leftrightarrow 2\text{H}_2 + \text{C} \quad \Delta H = 75 \text{ kJ.mol}^{-1} \quad (3) \\
2\text{CO} & \leftrightarrow \text{CO}_2 + \text{C} \quad \Delta H = -172 \text{ kJ.mol}^{-1} \quad (4)
\end{align*}
\]

The Ni based catalyst is commonly used in the DRM due to its high activity, low cost and availability [10–12]. However, the deactivation caused by carbon deposition still occurs on this catalyst. Many published works have reported the development of Ni catalysts to maintain high activity and show high resistance to carbon [13–15]. These are dependent on many factors such as nickel dispersion, supports, promoters, conditions for the catalyst preparation and the chemical interaction between nickel and the support [16–18]. Among these factors, types of the support are important to improve the DRM activity and stability of Ni catalysts [18–20]. Currently, many oxide supported Ni such as Ni/γ-Al$_2$O$_3$ [21], Ni/SiO$_2$ [22], and Ni/La$_2$O$_3$ [23] have been investigated. For Ni/Al$_2$O$_3$ and Ni/SiO$_2$, both CH$_4$ and CO$_2$ were activated on the same metal active sites as proposed by mono-functional mechanism and therefore the reaction rates were decreased [24]. On the other hand, the bi-functional mechanism was proposed for the Ni/La$_2$O$_3$ catalyst. The CH$_4$ dissociation occurred on Ni nanoparticles whereas the CO$_2$ activation occurred on La$_2$O$_3$ support [25]. The La$_2$CO$_3$ phase was formed by reaction of the CO$_2$ reactant and the La$_2$O$_3$ support. The Ni/γ-Al$_2$O$_3$ and Ni/La$_2$O$_3$ catalysts were compared in the work of Al-Fatesh et al. [21]. They speculated that the Ni/La$_2$O$_3$ catalyst showed higher stability during the DRM for a long time because the formation of La$_2$O$_3$CO$_3$ phase enhanced the adsorption of CO$_2$. The La$_2$O$_3$CO$_3$ phase can also inhibit coke formation by the creation of carbonates or oxycarbonates during the reaction [26]. However, a main problem of the Ni/La$_2$O$_3$ catalyst was poor dispersion of active Ni metals on the La$_2$O$_3$ due to low surface area [27].

In order to solve this problem, mineral-type precursor was introduced into the support to obtain high Ni dispersion through the formation of special structure [28–30]. Examples of this structure were perovskite [17], spinel [31], and fluorite [32]. Numerous research works have been published regarding high activity and stability for the DRM on the LaNiO$_3$ perovskite materials [33–35]. Oliveira et al. [33] reported the synthesis of a LaNiO$_3$ perovskite by a single step using chitosan as a chelating agent. This method showed the formation of 95% of the LaNiO$_3$ phase. They found that this catalyst showed high CH$_4$ and CO$_2$ conversions and good yields of CO and H$_2$. Chiarello et al. [36] reported the preparation of a LaCoO$_3$ perovskite by a single step FSP synthesis. The mechanism of perovskite formation by the FSP method was dependent on system condition, solvent volatility and lattice energies. These affected structure, particle size, thermal stability temperature [36,37]. Moreover, the LaCoO$_3$ perovskite structure can be modified by substitution of transition metals (Zn, Cu, Fe, Cr, Mn, or others) for Co sites. The transition metals have variable oxidation states and therefore they can change the oxygen mobility within the crystal lattice of the supported catalyst [38,39]. Touahra et al. [40] studied cooperation of Ni metal and LaCuO$_3$ perovskite support for the DRM. The LaCuO$_3$ perovskite supported NiO catalyst showed high catalytic activity and stability during the DRM compared to a LaCuO$_3$ perovskite catalyst. From the above information, we are interested in the mixed oxides consisting of the transition metals and La$_2$O$_3$ to be the catalyst support for the DRM. In this work, four transition metals Co, Mn, Zn and Cu were studied. This catalyst supports were synthesized by the flame spray pyrolysis (FSP). The Ni-based catalyst supported on the FSP-made material was evaluated in the DRM.

Figure 1. Scheme of equipment of flame spray pyrolysis (FSP).

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2. Materials and Methods

2.1 Material Preparation

The support material consisting of transition metal and lanthanum was synthesized by flame spray pyrolysis. The FSP equipment is shown in Figure 1. The precursors of four transition metals were cobalt(II) nitrate hexahydrate (Co(NO₃)₂.6H₂O), manganese(II) nitrate tetrahydrate (Mn(NO₃)₂.4H₂O), copper(II) nitrate trihydrate (Cu(NO₃)₂.3H₂O) and zinc nitrate hexahydrate (Zn(NO₃)₂.6H₂O). The lanthanum(III) nitrate hexahydrate (La(NO₃)₃.6H₂O) was used as the precursor of lanthanum. Both precursors were diluted by ethanol and fed into the center of a CH₄/O₂ flame using a syringe. The fine spray was formed by a capillary tip and evaporated into the flame. The dispersed oxygen was used in order to ensure the complete oxidation during the FSP step. The support material was collected on a glass microfiber filter with the aid of a vacuum pump. The Ni-based catalyst was prepared by incipient wetness impregnation (IWI). The nickel nitrate (Ni(NO₃)₂) aqueous solution was impregnated into the FSP-made support. The Ni loading was fixed as 2 wt%. The sample was kept at ambient temperature for 6 h and then dried at 110 °C for 12 h. Finally, the catalyst was calcined in air flow at 800 °C for 4 h. This catalyst was addressed as Ni/X-La₂O₃ when X symbol was transition metal (X = Co, Mn, Cu or Zn). The 30 wt% of transition metal based on the whole support was fixed in this work.

2.2 Material Characterization

The XRD measurement was used for identification and quantification of minerals, compounds and other crystalline phases of the catalyst. It was conducted on X-ray diffractometer SIEMENS D-5000 with a Cu Kα radiation source. The intensity data was recorded over a 2θ range of 20°–80° with a step size of 0.01° and with a scanning rate of 2°/min.

The specific surface area and the pore characteristics of the catalyst were determined by N₂ physisorption. The BET measurement was performed by BELSORP MINI II. Before the measurement, the catalyst was pretreated using He gas flow. The volume of adsorbed N₂ was measured at −196 °C using the different N₂ partial pressure.

The relative amount of active metals on the catalyst surface was estimated by H₂ chemisorption technique using a Micromeritics Pulse Chemisorb 2910 instrument. A 0.1 g of the catalyst sample was placed in a quartz U-shape reactor. Before the chemisorption step, the catalyst was reduced at 500 °C for 2 h. A 100 μl of the H₂ gas was injected into the catalyst at room temperature until saturation. The metal active sites were calculated from the volume of H₂ injected into the catalyst.

The reduction behavior of the catalyst was investigated by temperature programmed reduction with H₂ (H₂-TPR) using a Micrometrics Pulse Chemisorb 2910 instrument. A 0.1 g of the catalyst sample in a quartz U-shape reactor was reduced under a 30 ml/min of 10% H₂/N₂ gas flow from 100 to 800 °C. The water produced during the reduction was trapped by the liquid nitrogen.

Thermogravimetric analysis (TGA) was performed by SDT Q600 equipment. The catalyst was heated from room temperature up to 1000 °C in a heating rate of 10 °C/min under an air flow to measure loss of the catalyst weight.

2.3 Material Testing

The catalyst material was evaluated by the DRM. This reaction was occurred in a quartz tubular reactor under atmospheric pressure. A 0.3 g of the catalyst was packed in this reactor. The gas reactant was CH₄ and CO₂ with a molar ratio of unity. Prior to the catalytic testing, the temperature was raised to 700 °C in Ar flow and then the catalyst was reduced by H₂ flow at 500 °C for 2 h. After the reduction, the reactor temperature was increased to 700 °C in Ar flow and the gas reactant with GHSV of 18,000 h⁻¹ was introduced. The composition of the outlet stream was analyzed by gas chromatograph (GC) using Porapak Q column connecting with TCD detector. The catalytic activity and the product yield were reported to show the catalytic performance in the DRM. The CH₄ and CO₂ conversions, H₂/CO ratio, and H₂ yield were calculated by formulae as follows:

\[
\text{CH}_4 \text{ conversion} (\%) = \frac{\text{mole of CH}_4\text{ in} - \text{mole of CH}_4\text{ out}}{\text{mole of CH}_4\text{ in}} \times 100
\]

\[
\text{CO}_2 \text{ conversion} (\%) = \frac{\text{mole of CO}_2\text{ in} - \text{mole of CO}_2\text{ out}}{\text{mole of CO}_2\text{ in}} \times 100
\]

\[
\text{H}_2 \text{ yield} (\%) = \frac{\text{mole of H}_2\text{ out}}{2 \times \text{mole of CH}_4\text{ in}} \times 100
\]

\[
\text{H}_2/\text{CO ratio} = \frac{\text{mole of H}_2\text{ out}}{\text{mole of CO}_{\text{out}}}
\]
3. Results and Discussion

3.1 The Roles of Transition Metal in the Ni-based Catalysts

The physical, chemical and catalytic properties of this catalyst are reported. The crystal-line structure of the synthesized catalyst materials was investigated by X-ray diffractometer as shown in Figure 2. It was found that the Ni/Co-La₂O₃ and Ni/Mn-La₂O₃ catalysts showed the perovskite structure of LaCoO₃ and LaMnO₃, respectively [41,42]. This confirmed that the FSP method can be an efficient way to produce the perovskite-structure material. The Mn and La metals can easily form this structure consistent with the literatures [43,44]. A rapid quench at high temperature during flame process helped in an interaction between two metal oxides of the support and an maintenance of vacancies in the perovskite structure [45].

Schematic illustration of an example of the formation of LaCoO₃ perovskite structure during the FSP process is shown in Figure 3. As a high resolution of the XRD main peak between 31° and 35° (2θ scale) for the Ni/Co-La₂O₃ and Ni/Mn-La₂O₃ catalysts shown in Figure 4(a), the position of the main peak of the Ni/Mn-La₂O₃ was shifted more than that of the Ni/Co-La₂O₃ due to the valence change of some Mn cation from +3 to +4. The unusual oxidation states were a mixture Mn³⁺/Mn⁴⁺ ions with higher Mn³⁺ content. This indicated that the Ni/Co-La₂O₃ created the rhombohedral perovskite while the Ni/Mn-La₂O₃ showed a mixture of orthorhombic and rhombohedral perovskite [44,46]. As shown in Figure 2, the Ni/Cu-La₂O₃ showed narrow peaks of La₂CuO₄ spinel and CuO phase matching well with the reported data in literature [31]. The La₂CuO₄ (La₂O+La₃CuO₃) spinel belonged to the perovskite family, which the A site (La³⁺) had a larger metal cation than the B site (Cu²⁺). The La₂CuO₄ spinel, a mixture of LaO and LaCuO₃, belonged to the perovskite family, which the A site (La³⁺) had a larger metal cation than the B site (Cu²⁺). This structure had a lot of attention as a superconducting material [47,48]. When the zinc was introduced into the FSP-made support, a mixed phase of La₂O₃, ZnO and La(OH)₃ was apparent. It was indicated that Zn was inconstant in the perovskite structure under these conditions. The work by Moradi et
al. [49] reported the formation LaNiO$_3$ rhombohedra structure of LaNi$_{0.8}$Zn$_{0.2}$O$_3$ catalyst. When increasing the Zn loading by 0.6, it showed the three phases instead of the perovskite structure (LaNiO$_3$), which corresponded to the lanthanum oxide (La$_2$O$_3$), nickel lanthanum oxide (La$_2$NiO$_4$) and zinc oxide (ZnO) phases. Figure 4(b) shows the XRD patterns of the Ni/Co-La$_2$O$_3$ and Ni/Mn-La$_2$O$_3$ catalysts after testing the DRM at 700 °C for 15 h. The La$_2$O$_2$CO$_3$ phase was clearly apparent because the La$_2$O$_3$ reacted with the CO$_2$ reactant during the DRM. It was also remarked that the Ni/Co-La$_2$O$_3$ spent catalyst showed very high intensity of the XRD peak. The La$_2$O$_2$CO$_3$ phase could inhibit carbon formation on the catalyst surface [26]. Valderrama et al. [12] also reported that a mixed phase of La$_2$O$_2$CO$_3$, MnO and Mn$_2$O$_3$ was found on the Ni/Mn-La$_2$O$_3$.

Table 1 shows the data of N$_2$ physisorption and H$_2$ chemisorption. The BET surface area of four catalysts was in a range of 3.4–12.8 m$^2$/g. The Ni/Mn-La$_2$O$_3$ showed the highest surface area, which was close to the value of 11.0 m$^2$/g.

| Catalyst       | Structure           | $S_{\text{BET}}$ (m$^2$/g) | Pore volume (cm$^3$/g) | H$_2$ chemisorption ($\times 10^{18}$ atom/g catalyst) |
|----------------|---------------------|-----------------------------|------------------------|------------------------------------------------------|
| Ni/Co-La$_2$O$_3$ | LaCoO$_3$ perovskite | 3.4                         | 0.005                  | 13.3                                                 |
| Ni/Mn-La$_2$O$_3$ | LaMnO$_3$ perovskite | 12.8                        | 0.075                  | 4.8                                                  |
| Ni/Cu-La$_2$O$_3$ | spinel              | 3.4                         | 0.016                  | 0.7                                                  |
| Ni/Zn-La$_2$O$_3$ | La$_2$O$_3$, ZnO, La(OH)$_3$ | 8.4                         | 0.036                  | 1.2                                                  |

Figure 5. H$_2$-TPR profiles of (a) Ni/Co-La$_2$O$_3$ and Ni/Cu-La$_2$O$_3$ catalysts, (b) more intense peaks of Ni/Mn-La$_2$O$_3$ and Ni/Zn-La$_2$O$_3$ catalysts.
reported in the other work [12]. The \( \text{N}_2 \) adsorption/desorption isotherm was not shown here. However, it was found that for four catalysts the same pattern of the typical type-II isotherms was identified. These isotherms were unrestricted monolayer-multilayer adsorption indicating the existence of non-porous or macro-porous characteristics [50]. The metal active sites of the catalysts were measured by \( \text{H}_2 \) chemisorption. It was found that the \( \text{Ni/Co-La}_2\text{O}_3 \) exhibited the highest active sites. It was notable that \( \text{H}_2 \) can chemisorb on both Co and Ni active sites. This indicated the dual-sites adsorption of Ni and Co metals. On the other hand, a small amount of chemisorbed \( \text{H}_2 \) on the three other catalysts was observed. This was well known that the \( \text{H}_2 \) was weakly chemisorbed on Mn and Cu metal sites and it was not absorbed on Zn metallic sites [51]. Therefore, the results of \( \text{H}_2 \) chemisorption for three catalysts were implied to the Ni metallic sites on the catalyst surface. An order of \( \text{H}_2 \) chemisorption of three catalysts related to the BET surface area of them. It was remarked that the \( \text{Ni/Cu-La}_2\text{O}_3 \) and \( \text{Ni/Zn-La}_2\text{O}_3 \) catalysts showed very low active sites. Jalali et al. [52] also reported that a large crystallite size of Ni metal was found on the \( \text{Ni/CuAl}_2\text{O}_4 \) and \( \text{Ni/ZnAl}_2\text{O}_4 \) catalysts.

The \( \text{H}_2 \)-TPR profiles of all catalysts are presented in Figure 5. Because of very low intensity of \( \text{H}_2 \) consumption for the \( \text{Ni/Mn-La}_2\text{O}_3 \) and \( \text{Ni/Zn-La}_2\text{O}_3 \) catalysts, the TPR profile signal of these catalysts was adjusted to be 40 times of that of the \( \text{Ni/Co-La}_2\text{O}_3 \) and \( \text{Ni/Cu-La}_2\text{O}_3 \) catalysts. The \( \text{Ni/Co-La}_2\text{O}_3 \) exhibited the two reduction regions at below and above 520 °C. This was due to the reduction of \( \text{NiO, Co}_3\text{O}_4 \) and \( \text{La-CoO}_3 \). It was believed that the \( \text{Co}_3\text{O}_4 \) phase was present on the catalyst surface because the cobalt content in the catalyst was more than the stoichiometric ratio of the \( \text{La-CoO}_3 \) formation. Three steps of \( \text{La-CoO}_3 \) reduction were proposed by the other works [4,9,26] as shown in the following equations.

\[
\text{LaCoO}_3 + 0.25\text{H}_2 \rightarrow \text{LaCoO}_2.75 + 0.25\text{H}_2\text{O} \quad (9) \\
4\text{LaCoO}_2.75 + \text{H}_2 \rightarrow \text{La}_2\text{Co}_4\text{O}_{10} + \text{Co} + \text{H}_2\text{O} \quad (10) \\
\text{La}_2\text{Co}_3\text{O}_{10} + 4\text{H}_2 \rightarrow 2\text{La}_2\text{O}_3 + 3\text{Co} + 4\text{H}_2\text{O} \quad (11)
\]

At below 520 °C, the results could be attributed to the reduction of \( \text{NiO} \) to metallic Ni with concomitant formation of \( \text{La-CoO}_2.75 \) and \( \text{La-CoO}_2.75 \) from Equations (9) and (10), respectively. It was noted that the reduction temperature of a bulk NiO was normally about 350 °C. At above 520 °C, the reduction by Equation (11) was proposed to represent a strong interaction between metallic Co and \( \text{La}_2\text{O}_3 \) support. However, it was unclear about the reduction temperature of \( \text{Co}_3\text{O}_4 \) species. From the previous work [53], it was indicated that the \( \text{Co}_3\text{O}_4 \) formed by the FSP technique was reduced by \( \text{H}_2 \) in a wide temperature range of 150–750 °C. If the reduction by \( \text{H}_2 \) followed the Equations (9) and (10), the theoretical ratio of \( \text{H}_2 \) consumption at below and above 520 °C could be equal to 0.5. From the deconvolution of TPR profile, the ratio of \( \text{H}_2 \) consumption at low and high temperatures was about 0.4 and therefore it was possible that most of the \( \text{Co}_3\text{O}_4 \) were reduced at above 520 °C. The TPR profile of the \( \text{Ni/Cu-La}_2\text{O}_3 \) showed two reduction regions. The first region at below 300 °C indicated a sharp peak with a low-temperature shoulder. The very small broad peaks were observed in a high temperature range. All of the peaks in both regions could be attributed to the reduction of \( \text{NiO, La}_2\text{CuO}_4 \) and segregated \( \text{CuO} \). The XRD results in Figure 2 confirmed the presence of two latter species. The \( \text{CuO} \) was generally reduced by two reduction steps at low temperatures [54]. It was possible that the \( \text{CuO} \) was first reduced to \( \text{Cu}_2\text{O} \) and then to \( \text{Cu}^0 \) in the first region. The reduction of \( \text{La}_2\text{CuO}_4 \) was explained by Velasquez et al. [55]. They proposed the partial reduction of \( \text{La}_2\text{CuO}_4 \) to form \( \text{LaCuO}_{2.8} \) and \( \text{Cu}_2\text{O} \) at 230–320 °C and subsequently the \( \text{LaCuO}_{2.8} \) and \( \text{Cu}_2\text{O} \) were reduced at 420–550 °C. This suggestion was coincident with our results. It was also postulated that some of \( \text{H}_2 \) consumption in the second region was obtained by the reduction of \( \text{NiO} \) to \( \text{Ni}^0 \).

The \( \text{Ni/Mn-La}_2\text{O}_3 \) and \( \text{Ni/Zn-La}_2\text{O}_3 \) catalysts demonstrated very low intensity of \( \text{H}_2 \) consumption compared with the \( \text{Ni/Co-La}_2\text{O}_3 \) and \( \text{Ni/Cu-La}_2\text{O}_3 \) catalysts. This was due to a difficult reduction of \( \text{LaMnO}_3 \) perovskite and \( \text{ZnO} \). The \( \text{Ni/Mn-La}_2\text{O}_3 \) showed a main peak between 300–400 °C. It was clear that the reduction of \( \text{NiO} \) to \( \text{Ni}^0 \) was occurred in this temperature range. It was possible that the reduction of \( \text{MnO}_2 \) and some of \( \text{LaMnO}_3 \) perovskite-like structure was also occurred. Although the \( \text{MnO}_2 \) was not found by the XRD analysis as shown in Figure 2, it can be formed during the FSP step like the formation of \( \text{Co}_3\text{O}_4 \) in the \( \text{Ni/Co-La}_2\text{O}_3 \) as discussed above. At low temperature, the reduction of \( \text{Mn}^{4+} \) to \( \text{Mn}^{3+} \) was declared while the reduction of \( \text{Mn}^{3+} \) to \( \text{Mn}^{2+} \) was assigned at high temperatures [44]. These were consistent with the signal of \( \text{H}_2 \) consumption in a range of 300–400 °C and above 600 °C, respectively. The reduction of \( \text{LaMnO}_3 \) perovskites was a complex process. This occurred in a wide temperature range of 200–900 °C as
They suggested that La$_2$O$_3$, La(OH)$_3$ and MnO species were formed after the reduction of LaMnO$_3$. It was possible that the lanthanum manganite was also reduced in this work. The presence of MnO was confirmed by the XRD results of the spent catalysts as shown in Figure 4(b). It was indicated that the MnO obtained by H$_2$ reduction was stable under the reaction condition. Besides, the appearance of the MnO$_3$ phase in the spent catalyst exhibited the reduction of either MnO$_2$ species or other forms of perovskites such as the La$_{0.95}$MnO$_3$ structure proposed by the literature [12]. In the case of Ni/Zn-La$_2$O$_3$, a very small reduction peak at 300 °C was implied as the reduction of NiO to Ni$^0$. The results of the H$_2$ chemisorption form Table 1 and this TPR profile indicated a very small amount of Ni metallic sites on the catalyst surface. It was possible that in this case some of nickel and ZnO could generate the NiZn alloy during the preparation of the catalyst although this alloy was not found by the XRD. The reduction peak at above 500 °C was attributed to the reduction of ZnO to metallic zinc [56] or the NiO interacted strongly with ZnO in the NiZn alloy [57].

The four catalysts were evaluated by the DRM reaction at 700 °C for 15 h. The CH$_4$ conversion and the molar ratio of H$_2$ and CO in the product were plotted with time on stream as shown in Figure 6. The reaction behaviors of the Ni/Co-La$_2$O$_3$ were different from the three other catalysts. This was an increase of the catalytic activity of the Ni/Co-La$_2$O$_3$ with increasing time during 1–7 h. Before the reaction test, this catalyst was reduced by H$_2$ at 500 °C for 2 h. At this temperature, the reduction of the La$_{2}$Co$_{10}$ and some CoO$^4$ strongly interacted with the support was incomplete as confirmed by the TPR results in Figure 5(a). Hence, during the DRM reaction at 700 °C, the La$_{2}$Co$_{10}$ and CoO$^4$ species were gradually reduced by the H$_2$ produced from the reaction resulting in an increase of metallic active cobalt sites on the catalyst surface. The complete reduction was expected in 7 h and a change of CH$_4$ conversion was significantly observed. After 7 h, for all catalysts the CH$_4$ conversion and the H$_2$/CO ratio in the product stream remained constant indicating no deactivation due to coking. This was because the formation of La$_{2}$O$_3$CO$^8$ phase during the reaction test could inhibit carbon formation on the catalyst surface. The presence of this phase on the spent catalysts was confirmed by the XRD results in Figure 4(b). Figure 7 shows the comparable results of the two reactant conversions and the H$_2$ product yield of the DRM reaction at 700 °C for 15 h. For all four catalysts, the CO$_2$ reactant was converted more than the CH$_4$ indicating an occurrence of the reverse water-gas shift reaction (RWGS). Hence, the obtained H$_2$/CO molar ratios were lower than the stoichiometric ratio. The Ni/Co-La$_2$O$_3$ exhibited the highest conversions, H$_2$ product yield and H$_2$/CO product ratio. It was noted that the catalytic activity of the Co-La$_2$O$_3$ support was also collected but not shown here. This support showed less than 10% of both CH$_4$ and CO$_2$ conversions. Therefore, a cooperative effect of the Ni and Co metal active sites on the La$_2$O$_3$ matrix was nec-

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**Figure 6.** (a) CH$_4$ conversion and (b) H$_2$/CO ratio of Ni/Co-La$_2$O$_3$, Ni/Mn-La$_2$O$_3$, Ni/Cu-La$_2$O$_3$ and Ni/Zn-La$_2$O$_3$ catalysts in DRM at 700 °C for 15 h.

**Figure 7.** CH$_4$ and CO$_2$ conversions and H$_2$ yield of Ni/Co-La$_2$O$_3$, Ni/Mn-La$_2$O$_3$, Ni/Cu-La$_2$O$_3$ and Ni/Zn-La$_2$O$_3$ catalysts in DRM at 700 °C, 15 h.
necessary to activate the reactant in this case. The Ni/Mn-La$_2$O$_3$ and Ni/Cu-La$_2$O$_3$ catalysts showed moderate catalytic activity in the same level. However, the different mechanisms were proposed. For the Ni/Mn-La$_2$O$_3$, the metal active sites were only dispersed metallic Ni particles. The Mn and La species were in oxide forms. It was speculated that the segregated Mn$_2$O$_3$ and MnO with small particle size retarded agglomeration of impregnated Ni resulting in a high dispersion of Ni active sites measured by H$_2$ chemisorption as shown in Table 1. The Ni metal, MnO particle and La$_2$O$_3$ support was key components to activate the CH$_4$ and CO$_2$ reactants for the DRM reaction in this case. The MnO can react with CO$_2$ to produce MnO$_2$ and CO [58]. In addition, the carbon deposits can be also removed by the MnO$_2$ as shown in the following Equations (12) and (13) [59]:

$$\text{CO}_2 + \text{MnO} \rightarrow \text{CO} + \text{MnO}_2$$  \hspace{1cm} (12)  
$$\text{C} + \text{MnO}_2 \rightarrow \text{CO} + \text{MnO}$$  \hspace{1cm} (13)  

For the Ni/Cu-La$_2$O$_3$, a low amount of Ni active sites can maintain a promising catalytic activity. It was speculated that the Cu metal, which was obtained by the reduction of CuO at low temperatures, had an important role to activate CH$_4$ as well. In this case, the synergistic effect of Ni and Cu metals was a key factor to catalyze the DRM. The Ni/Zn-La$_2$O$_3$ showed the lowest activity due to a low amount of metallic Ni active sites. The ZnO on the catalyst surface was inactive to the DRM reaction. However, the presence of the NiZn alloy was expected to have a promotional effect on the activity and stability consistent with the work of Masoom Nataj et al. [60].

Figure 8 shows TG weight and DTG profiles of the spent catalysts under air flow. These catalysts were obtained from the DRM reaction test at 700 °C for 15 h. The TG results exhibited weight losses in two temperature ranges. As reported by Lima et al. [14], the weight loss in a range of 300 and 550 °C represented the oxidation of the carbon deposits while the weight loss at about 800 °C suggested the decomposition of La carbonates. The Ni/Zn-La$_2$O$_3$ presented the highest DTG intensity and TG weight loss at 49.5% as shown in Table 2. This implied high amount of coke on the catalyst surface affecting very low activity. The Ni/Mn-La$_2$O$_3$ showed the TG weight loss lower than the Ni/Co-La$_2$O$_3$. From the XRD results in Figure 4(b), the mixed phases of La$_2$O$_3$CO$_3$, MnO and Mn$_2$O$_3$ were present in the Ni/Mn-La$_2$O$_3$. Besides the La$_2$O$_3$CO$_3$, the MnO species can move the carbon deposits on the catalyst surface as shown above in Equations (12) and (13). While the coke formation on the Ni/Co-La$_2$O$_3$ catalyst was inhibited by only La$_2$O$_3$CO$_3$ species. The Ni/Cu-La$_2$O$_3$ showed a small amount of coke on the catalyst surface. An increase of TG weight in a wide range of temperature was due to the re-oxidation of Cu$^+$ to Cu$^{2+}$, which occurred at a temperature of 300–700°C [17]. The weight loss in the temperature range of 750–1000 °C was the carbonaceous deposits and presented 2.6 wt.% [55].

### 3.2 The Partial Substitution of Co for Mn into the Ni/Co-La$_2$O$_3$ Catalyst

The Ni/Co-La$_2$O$_3$ was a promising candidate to catalyze the DRM. It showed high product yield of H$_2$ and had no deactivation in 15 h. However, a significant amount of carbon deposits reported by the above TG results may possibly cause deactivation by prolonging the reaction time. To solve this problem, it was interesting to study the partial substitution of Co for Mn because the MnO can remove the carbon on the catalyst surface together with the La$_2$O$_3$CO$_3$ as discussed above. In this case, the

| Catalyst       | Weight loss TG after reaction (%) |
|----------------|----------------------------------|
| Ni/Co-La$_2$O$_3$ | 23.2                             |
| Ni/Mn-La$_2$O$_3$ | 12.3                             |
| Ni/Cu-La$_2$O$_3$ | 2.6                              |
| Ni/Zn-La$_2$O$_3$ | 49.5                             |

Table 2. The weight loss of spent catalysts in DRM at 700 °C for 15 h.
Co, Mn and La precursors were simultaneously fed into the flame to synthesize the FSP-made supports. These supports were addressed as MnCo1–xLa2O3 when x meant a molar fraction of Mn in the mixture of Mn and Co. Three supports were synthesized in this work. Two of them were loaded by low Mn content (x = 0.05 and 0.1) and another was an equimolar mixture of Mn and Co. A 2 wt% Ni was loaded on the MnCo1–xLa2O3 support by incipient wetness impregnation method and then the Ni-based catalysts were calcined in air flow at 800 °C for 4 h. The X-ray diffraction spectra of samples with different Mn doping are shown in Figure 9. The X-ray diffraction spectra of three catalysts with co-doped Co and Mn are compared to those of the Ni/Co-La2O3 and Ni/Mn-La2O3 catalysts as shown in Figure 9(a). The partial substitution can maintain the perovskite-type structure consistent with the literatures [61,62]. The crystal spacing calculated by Bragg equation was slightly increased with increasing the Mn content. Figure 9(b) shows the different position of the XRD main peak at 32–34°. This was indicated that the Mn ion partly entered into the perovskite-type structure by replacing the Co ion. An increase of Mn-substitution amounts exhibited the peak shift to lower 2θ since the ionic radius of Mn3+ (0.645 Å) was larger than that of Co3+ (0.545 Å). From the XRD results, it was also remarked that the coexistence of rhombohedral and orthorhombic phases was apparent in the MnCo1–xLa2O3 support dependent on the degree of Mn substitution [12,44].

Figure 10 shows the H2-TPR profiles of the Ni/MnCo1–xLa2O3 catalysts. As compared to the Ni/Co-La2O3, the reduction peaks at below 520 °C were shifted to lower temperature and the area of these peaks was varied by the substituted Mn content. While a new broad reduction peak was apparent at above 700 °C. This was because Mn with high valence was inserted into the perovskite structure resulting the reduction of some Co3+ to Co2+ [46]. At low temperature, the Co3+, MnO2 and NiO particles formed during the FSP step and dispersed on the catalyst surface were mainly reduced. At high temperature, the reduction of lattice oxygen ion in the perovskite structure was proposed. It was speculated that the strength of Co–O–Co bond was weaken compared to Co–O–Mn and Mn–O–Mn bonds. This was implied that the reduction peak at 600 °C was attributed to Co–O–Co bond while the broad peak at above 650 °C was related to Co–O–Mn and Mn–O–Mn bonds. From the TPR results, it was implied that the Ni/Mn0.05Co0.95-La2O3 and Ni/Mn0.5Co0.5-La2O3 catalysts showed more Co–O–Co and more Co–O–Mn bonds, respectively, while the Ni/Mn0.1Co0.9-La2O3 consisted of both Co–O–Co and Co–O–Mn within the crystal lattice. It was also noted that the Ni/Mn0.1Co0.9-La2O3 catalyst showed a high amount of reduced H2. This was possible that more Mn entered into the perovskite structure and therefore excess Co became more Co3+ particles dispersed on the catalyst surface. The

Figure 9. XRD patterns of Ni/Co-La2O3, Ni/Mn0.05Co0.95-La2O3, Ni/Mn0.1Co0.9-La2O3, Ni/Mn0.5Co0.5-La2O3 and Ni/Mn-La2O3 catalysts (a) as prepared and (b) more intense peaks.

Figure 10. TPR profiles of Ni/Co-La2O3, Ni/Mn0.05Co0.95-La2O3, Ni/Mn0.1Co0.9-La2O3, Ni/Mn0.5Co0.5-La2O3 and Ni/Mn-La2O3 catalysts.

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CoO₄ formed during the FSP step can be reduced at both low and high temperatures [53].

The results of DRM reaction at 700 °C for 15 h were reported in Figures 11 and 12. It was found that the Ni/Mn₀.₀₅Co₀.₉₅La₂O₃ catalyst showed the highest CH₄ conversion, H₂ yield and H₂/CO ratio. This catalyst can maintain the activity and product yield for 15 h. This was suitable content of Mn inserted into the perovskite structure to change the oxygen mobility within the crystal lattice of the Co component. Both the Ni/Mn₀.₁Co₀.₉₅La₂O₃ and the Ni/Mn₀.₅Co₀.₅La₂O₃ catalysts showed a significant decrease of the CH₄ conversion. A large amount of CoO₄ particles in the Ni/Mn₀.₁Co₀.₉₅La₂O₃ catalyst confirmed by the TPR result was possible to accelerate the coke formation and therefore the DRM activity was dropped. On the other hand, for the Ni/Mn₀.₅Co₀.₅La₂O₃ catalyst more Co–O–Mn bond in the crystal lattice can inhibit the formation of La₂O₂CO₃ phase resulting in high propagation rate of carbon. It was remarked that, low performance of the Ni/Mn-La₂O₃ catalyst was due to the distortion of non-rhombohedral perovskite symmetry and the effect of the reverse water-gas shift reaction [63].

Figure 13 shows the XRD signal of the spent catalysts. The La₂O₂CO₃ phase was apparent due to the La₂O₃ reacting with the CO₂ reactant during the DRM. This phase can inhibit carbon formation and improve the catalytic activity and stability of the DRM reaction [3,64,65]. The highest intensity of the La₂O₂CO₃ phase was found by the Ni/Co-La₂O₃ catalyst. The segregated CoO₄ phase was formed on the catalyst surface of the Ni/Mn₀.₀₅Co₀.₉₅La₂O₃ catalyst. This was because the Co metal ion was substituted for Mn metal ion. However, the MnOₓ phase disappeared due to a low amount of Mn. The Ni/Mn₀.₁Co₀.₉₅La₂O₃ and the Ni/Mn₀.₅Co₀.₅La₂O₃ catalysts show only La₂O₂CO₃ phase but lower intensity of XRD peaks.

Figure 11. (a) CH₄ conversion and (b) H₂/CO ratio of Ni/Co-La₂O₃, Ni/Mn₀.₀₅Co₀.₉₅La₂O₃, Ni/Mn₀.₁Co₀.₉₅La₂O₃, Ni/Mn₀.₅Co₀.₅La₂O₃ and Ni/Mn-La₂O₃ catalysts in dry reforming of methane at 700 °C for 15 h.

Figure 12. CH₄ and CO₂ conversion and H₂ yield of Ni/Co-La₂O₃, Ni/Mn₀.₀₅Co₀.₉₅La₂O₃, Ni/Mn₀.₁Co₀.₉₅La₂O₃, Ni/Mn₀.₅Co₀.₅La₂O₃ and Ni/Mn-La₂O₃ catalysts in DRM at 700 °C, 15 h.

Figure 13. XRD patterns of Ni/Co-La₂O₃, Ni/Mn₀.₀₅Co₀.₉₅La₂O₃, Ni/Mn₀.₁Co₀.₉₅La₂O₃, Ni/Mn₀.₅Co₀.₅La₂O₃ and Ni/Mn-La₂O₃ catalysts after test catalytic at 700 °C for 15 h.
Figure 14 and Table 3 show the TG and DTG results of the spent catalysts after testing the dry reforming of methane at 700 °C for 15 h. These results indicated a significant amount of carbon deposits on the catalyst surface through the TG peak in a range of 300–550 °C. As discussed above, both La2O3CO3 and MnO phases can inhibit the coke formation and therefore the Ni/Co-La2O3 and Ni/Mn-La2O3 catalysts showed a low amount of carbon deposits. For the same reason, the Ni/Mn0.05Co0.95-La2O3 catalyst had a low rate of coke formation. More dispersed CoO4 particles confirmed by the TPR results accelerated the propagation of coke on the surface of the Ni/Mn0.1Co0.9-La2O3 catalyst. For the Ni/Mn0.5Co0.5-La2O3 catalyst, much more Mn inserted into the perovskite structure can generate more Co–O–Mn bond in the lattice leading to the difficult formation of La2O3CO3 phase. A high rate of coke formation in both Ni/Mn0.1Co0.9-La2O3 and Ni/Mn0.5Co0.5-La2O3 catalysts from the TG and DTG results was related to a decrease of the DRM activity with time on stream as shown above.

4. Conclusions

The Ni catalysts supported on the FSP-made transition metal (Co, Mn, Cu or Zn) doped La2O3 materials were investigated. It was found that the Ni/Co-La2O3 and Ni/Mn-La2O3 catalysts showed the LaCoO3 and LaMnO3 perovskites, respectively. This confirmed that the FSP method can be efficient to produce the perovskite-structure material. The Ni/Co-La2O3 created the rhombohedral perovskite while the Ni/Mn-La2O3 showed a mixture of orthorhombic and rhombohedral perovskites. The La2CuO4 spinel and CuO phase was apparent in the Ni/Cu-La2O3 while a mixed phase of La2O3, ZnO and La(OH)3 was observed in the Ni/Zn-La2O3. High reducibility for the Ni/Co-La2O3 and Ni/Cu-La2O3 catalysts was related to the reduction of LaCoO3 and La2CuO4 phases. High activity for the DRM reaction on the Ni/Co-La2O3 was due to a cooperative effect of the Ni and Co metal active sites on the La2O3 matrix. A high dispersion of metallic Ni particles on the surface of the Ni/Mn-La2O3 and the dual sites of Ni and Cu on the Ni/Cu-La2O3 resulted in moderate DRM activity. On the other hand, the Ni/Zn-La2O3 showed low DRM activity due to the agglomeration of the Ni particles on the catalyst surface. Among four catalysts, the Ni/Mn-La2O3 was promising catalyst to remove the carbon deposits through the cooperation of La2O3CO3 and MnOx. The partial substitution of Co for Mn with a small content of Mn enhanced the catalytic performance of the DRM reaction. The highest CH4 conversion, H2 yield and H2/CO ratio were found in the Ni/Mn0.05Co0.95-La2O3 catalyst. However, an insertion of more Mn resulted in more Co being excluded from the perovskite structure and the CoO4 particles were formed on the catalyst surface leading to acceleration of coke formation.

Table 3. The weight loss of Ni/Co-La2O3, Ni/Mn0.05Co0.95-La2O3, Ni/Mn0.1Co0.9-La2O3, Ni/Mn0.5Co0.5-La2O3 and Ni/Mn-La2O3 spent catalysts in dry reforming of methane at 700 °C for 15 h.

| Catalyst                     | Weight loss (%) |
|------------------------------|-----------------|
| Ni/Co-La2O3                  | 23.2            |
| Ni/Mn0.05Co0.95-La2O3        | 18.4            |
| Ni/Mn0.1Co0.9-La2O3          | 36.7            |
| Ni/Mn0.5Co0.5-La2O3          | 37.1            |
| Ni/Mn-La2O3                  | 12.3            |
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