Abstract: In this paper, a comprehensive study was carried out on the application of perovskite catalyst in dry reforming of CH$_4$. The perovskite catalyst was prepared using a sol–gel method. The prepared samples were characterized by N$_2$ adsorption/desorption, TPR, XRD, CO$_2$-TPD, TGA, TPO, Raman, and SEM techniques. In addition, the effect of operating pressure, namely, 1 bar, 3 bar, 5 bar, and 7 bar, temperature (500–800 °C) was evaluated. The characterization results indicated that catalysts operated at 1 bar, gas hourly space velocity of 84000 (mL/g/h) gave the best catalytic performance. CH$_4$ and CO$_2$ conversions of 77 and 80% were obtained at 1 bar and at 700 °C reaction temperature. The increase of reaction temperatures from 500 °C to 800 °C increased the reaction rate and hence the methane and carbon dioxide conversions were increased. A unity ratio of H$_2$/CO was obtained at 1 bar for temperatures 600 °C and above. Similarly, the time on stream tests, obtained at a 700 °C reaction temperature, showed that the best ratio in terms of the closeness of unity and the stable profile could be attained when the pressure was set to 1 bar. The TGA analysis showed the drop of mass due to oxidation of carbon deposits, which started at 500 °C. The catalyst operated at 1 bar produced the least amount of carbon, equivalent to 35% weight loss, while the 3 and 5 bar operated catalysts generated carbon formation, equivalent to 65% weight loss. However, the 7 bar operated catalyst resulted the highest accumulation of carbon formation, equivalent to 83% weight reduction. Hence, the TGA profile indicated the relative carbon deposition on the catalyst, which was dependent of the operated pressure and hence confirmed the suitability operation pressure of 1 bar. The characterizations of the Raman, EDX, TGA, and TPO all presented the formation of carbon.

Keywords: Al; dry reforming; La; methane; Ni; perovskite; pressure
for Fischer–Tropsch (FT) synthesis to generate hydrocarbons [9,10]. The choice of proper catalyst plays an essential role in the catalytic activity and stability [11]. Transition metals such as Ni, Co are suitable for catalysing this process [12–14]. Ni based catalysts are often used due to their cheap price, abundance, and quick turnover rates [15]. Main difficulties encountered in using Ni-based catalysts come from the sintering which causes the loss of active metal surface areas and the carbon deposition on the surface, which deactivates and reduces the activity by covering the active metal surface and alters product selectivity [16].

Perovskites are used in catalytic and photovoltaic industries for their excellent performance. Perovskite structures containing Ni are employed for CO$_2$ reforming of CH$_4$. It has been depicted that perovskite-type oxides accomplish the need of high thermal stability and metal dispersion [17,18]. The use of perovskite oxides, where the B-site cation is a diluted transition metal such as Ni, has called for more research [19,20]. Ren et al. investigated the unexpected coke-resistant stability in steam-CO$_2$ dual reforming of methane over the robust Mo$_2$C-Ni/ZrO$_2$ catalyst [21]. Their results showed high catalytic activity and unexpected stability in steam-CO$_2$ dual reforming of CH$_4$ for syngas production. Alternatively, Ziaei-Azad et al. studied the influence of Pd on the enhancement of oxidation activity of LaBO$_3$ (B = Mn, Fe, Co, and Ni) perovskite catalysts for pollution abatement from natural gas fueled vehicles [22]. Their results indicated that Pd significantly enhanced the reducibility of B in LaBPD$_{0.05}$O$_3$ perovskites and improves the mobility of lattice oxygen in the prepared samples, which results in activity enhancement for Pd-containing catalysts. The work of Messaoudi et al. reports the investigation of LaxNiOy and LaxNiOy/MgAl$_2$O$_4$ catalysts in CO$_2$ reforming of methane [23]. The outcome exhibited higher specific surface areas and nickel dispersions of the supported catalysts and thus supported catalysts were found more active and stable with low carbon deposition. Ruocco et al. [24] investigated the influence of preparation techniques, reaction temperature and gas hourly velocity in dry reforming reaction using ternary perovskites-type oxides, AZrRuO$_3$ (A = Ca, Ba, Sr). They found SrZrRuO$_3$ catalyst provided the best results of conversion and stability. Whereas, Wang et al. [25] explored the use of bimetallic Ni-Co catalysts supported on La$_2$O$_3$-LaFeO$_3$ perovskite. The catalytic activity and coking resistance were enhanced by substituting a proper amount of Co. The crystalline structure of the perovskite also played a crucial role.

In this study, we investigated the performance of a typical perovskite catalyst (Na$_{0.5}$La$_{0.5}$Ni$_{0.3}$Al$_{0.7}$O$_{2.5}$) obtained using the sol gel technique. The effect of different reaction temperatures and pressures over the efficiency of the process was examined.

2. Results and Discussion

2.1. Catalyst Characterization

The surface texture of the catalyst was evaluated via the nitrogen adsorption–desorption isotherms. Figure 1A demonstrates the nitrogen adsorption isotherms of the unused catalysts calcined at 725 °C with BET surface area of 12.4 m$^2$/g, pore volume of 0.04 cm$^3$/g, pore diameter of 13 nm, according to IUPAC labelling, catalysts showing type IV isotherm with H$_1$ hysteresis loop [26]. While Figure 1B matches the distributions of pore size attained via BJH method. The pore size distribution depicts that most particles possess 140 nm particle diameters, which means macroporous characteristics. The H$_2$-TPR evaluations of the perovskite catalyst were done to disclose the removal of the oxygen behavior of various oxide species of nickel. As shown in Figure 1C, the H$_2$-TPR profile of the catalyst presents three peaks, the first one appeared around 332°C corresponding to the reduction of NiO species that barley interacted with the support. The second peak occurred at 653 °C, where NiO strongly interacted with the alumina support, and the third peak appeared at 744 °C with a maximum consumption of H$_2$ between 500 and 900 °C was ascribed to the reduction of intimately associated surface to nickel deposited on lanthanum and alumina oxides [27]. From the TPR result, it is apparent that the Ni interacts strongly with the support confirming the hydrothermal stability of perovskites. For the generation of CO from the adsorption and activation of CO$_2$, it is essential to perform the
basicity of the catalyst. The reactive O$_2$ species produced from CO$_2$ activation can assist the removal of the formed carbon on the catalyst [28]. In this study, CO$_2$-TPD was used to investigate the catalyst’s basicity. As depicted in Figure 1D, two small peaks in low temperature regions (100 °C and 280 °C) and intense peaks in high temperature regions about 760 °C. It is largely considered that the peaks at lower temperature regions can be credited to the weak basic sites resulting from the physical adsorption of CO$_2$ [29]. While the peak appearing at the high temperature relates to the strong basic sites attributed to the chemisorption of CO$_2$. As the result of the number of basic sites, peaks take different sizes [30]. It can be concluded that the catalyst is manifested by strong basic sites which enhances the adsorption of CO$_2$ on the catalyst surface.

![Figure 1](image_url)

**Figure 1.** (A) N$_2$ adsorption–desorption isotherms, (B) pore size distribution, (C) TPR, and (D) CO$_2$-TPD profile for fresh catalyst calcined at 725 °C.

The crystalline nature of Na$_{0.5}$La$_{0.5}$Ni$_{0.3}$Al$_{0.7}$O$_{2.5}$ catalysts was investigated by XRD, and the results are illustrated in Figure 2. The results revealed that the characteristic Bragg diffraction peaks at 2θ = 23.47, 32.96, 41.5, 48.4, 54.2, 59.5, and 63.3 are correlated well with the Al$_{0.5}$LaNi$_{0.5}$O$_{3.054}$ (Rhombohedral Crystal System, JCPDS NO: 01-083-0757) whereas peaks at 2θ = 37.3, 43.1 are correlating with Na$_5$NiO$_4$ (Orthorhombic Crystal System JCPDS-01-071-1988). The structural characteristic of elements well matched with standard data.
2.2. Catalytic Activity

The perovskite catalyst activated at 750 °C was researched in dry reforming at 700 °C reaction temperature and a gas hourly space velocity (GHSV) of 84,000 mL g\(^{-1}\) h\(^{-1}\). Figure 3 shows the time on stream of 8 h versus conversions of methane and CO\(_2\) for various pressures (1, 3, 5, 7 bar). The effect of the pressure is well denoted such that both methane and CO\(_2\) conversions assumed the highest values of 77% and 80% respectively, with % deactivation factor of 9.3, when 1 bar pressure was used. While the lowest conversions of 45% and 52.5% were recorded, with % deactivation factor of 10.9, when highest pressure of 7 bar was implemented. The stability is also affected by the increase of the pressure. For instance, at 5 bar the CH\(_4\) and CO\(_2\) conversion decreased from 58% and 55% to 45% and 50% respectively. On the other hand, Figure 4 displays the time on stream of hydrogen and CO ratios for 8 h when different pressures were used. The result indicates that the best ratio in terms to the closeness to unity and the stable value could be attained when the pressure was set to 1 bar. It can be deduced from this section that both stability and activity of the catalyst is significantly affected by the operating pressures.

Table 1 exhibits the CH\(_4\) conversion of this work and those in the literature. The achieved result compares well with the literature values, particularly those operated at similar reaction temperatures. The activity per gram obtained shows quite improvement in comparison.
Figure 3. TOS against (A) methane and (B) carbon dioxide conversions, for catalyst at 725 °C, 700 °C calcination and reaction respectively, 0.05 g catalyst, CH\(_4\) = 30 mL/min, CO\(_2\) = 30 mL/min, N\(_2\) = 10 mL/min, GHSV = 84000 (mL/g/h).

Figure 4. TOS against hydrogen and carbon monoxide ratios, for catalyst: calcination at 725 °C, activation at 750 °C, reaction at 700 °C, 0.05 g catalyst, CH\(_4\) = 30 mL/min, CO\(_2\) = 30 mL/min, N\(_2\) = 10 mL/min, GHSV = 84000 (mL/g/h).
Table 1. Comparison between the CH\(_4\) conversion obtained and those from data available in literature for different catalysts used in dry reforming of CH\(_4\)

| Catalyst                      | CH\(_4\):CO\(_2\) | GHSV (mL/g/h) | Catalyst weight (g) | T (°C) | %CH\(_4\) | References |
|-------------------------------|-------------------|---------------|---------------------|--------|-----------|------------|
| 1%Ru/ZrO\(_2\)-SiO\(_2\) 1:1 | 1:1               | 80000         | 0.03375             | 800    | 67        | [31]       |
| 1% Ru-Al\(_2\)O\(_3\)-MgO 1:1 | 1:1               | 16000         | 0.15000             | 700    | 74        | [32]       |
| CaZrRuO\(_3\) 1:1            | 1:1               | 36000         | 0.10000             | 700    | 60        | [24]       |
| La (Co\(_{0.1}\)Ni\(_{0.9}\))\(_{0.5}\)Fe\(_{0.5}\)O\(_3\) 1:1 | 1:1               | 12000         | 0.30000             | 750    | 72        | [25]       |
| Na\(_{0.5}\)La\(_{0.5}\)Ni\(_{0.3}\)Al\(_{0.7}\)O\(_3\) 1:1 | 1:1               | 84000         | 0.05000             | 700    | 77        | Present work |

Figures 4B and 5A,B show the effect of reaction temperature on methane and carbon dioxide conversions for pressures (1, 3, 5, and 7 bar). It is evident from the profiles that the conversions grew with the rise of the reaction temperature. This is expected as the DRM process is endothermic. The conversions operated at 1 bar pressure depicted an average improvement of 15% for moderate temperatures less than 750 °C. This means that the conversion values of 1 bar operated catalyst are higher than those operated at other pressures, where their conversion values are at least 15% less than that of 1 bar operated catalyst when the reaction temperature is higher than 650 °C and lower than 750 °C. The result of reaction temperatures displays the effect of operating pressure, where high pressures impede the activity.
Figure 5. Catalytic activities of perovskite catalyst calcined at 725 °C, using 0.05 g of catalyst and CH$_4$: CO$_2$:N$_2$ = 30/30/10 mL/min. at GHSV of 84000 mL/g/h at T = 500–800 °C. (A) CH$_4$ conversion, (B) CO$_2$ conversion.

Figure 6 depicts the effect of reaction temperature on hydrogen and CO ratios for pressures (1, 3, 5, and 7 bar). It is evident from the profiles that the ratio increases with the rise of the reaction temperature from 500 °C to 600 °C. This could be related to the endothermicity of the process. The highest value of H$_2$/CO is obtained at 600 °C for all operating pressures. The same effect was observed for dry reforming of methane over alumina-supported nickel catalysts for all Ni Loading [33]. The phenomenon was related to the fact that the highest carbon deposition was recorded at 600 °C. Beyond 600 °C, the ratio is either maintained at an almost constant value as in the case of 1 bar, or decreased as in the case of 7 bar where the ratio reduced by 26%. The H$_2$/CO ratio obtained at 1 bar pressure depicted a unity ratio for temperatures equal to or greater than 600 °C.

Stability test was performed on the catalyst over 30 h time on stream. The results obtained in Figure 7, shows that there is no significant loss of activity for the period under investigation. The reaction was performed at 1 bar, 700 °C and 84000 mL/g/h space velocity. The steady stability obtained symbolizes the constituents of the perovskite hinders the deactivation commonly seen with Ni based catalysts.

Catalysts’ morphology was examined using SEM as shown in Figure 8. In the fresh catalyst (Figure 8A) individual leaf-blade shapes are in majority but in used catalyst (Figure 8B,C) this identity vanishes. The coke deposition on the used catalyst is verified in EDX as well as in TGA results.

The identification of the types of carbon deposited over used catalysts in DRM is crucial in comprehending its deactivation behaviour. Thus, temperature programming oxidation (TPO) analysis is often carried out. Figure 9 displayed the TPO of the used perovskite in this work for four different pressures (1, 3, 5, and 7 bar). The TPO tests were performed with spent Na$_{0.5}$La$_{0.5}$Ni$_{0.3}$Al$_{0.7}$O$_{2.5}$ catalysts operated at 700 °C and lasted for 8 h of reaction. The TPO patterns demonstrated the presence of a single peak for each pressure with maxims at 500–620 °C. This can be assigned to polymeric respectively [34]. The type of coke represented here for high pressure was graphic carbon deposited on the support which metallic centre did not catalyse and removed at T > 650 °C [35] and this type of coke can be totally removed using pure O$_2$ at 700 °C. The TPO analysis discloses the formation of
amorphous carbon at 1 bar while high pressure forms graphitic carbon. The shifting of peaks toward high temperature denotes the growth tendency of graphitic carbon. The TPO analysis confirms the TGA analysis showing the increase formation of carbon deposit with the increase of pressure.

Figure 6. Catalytic activities of perovskite catalyst calcined at 725 °C, activated at 750 °C, using 0.05 g of catalyst and CH₄: CO₂:N₂ = 30/30/10 mL/min at GHSV of 84000 mL/g/h at T = 500–800 °C. Effect of hydrogen and carbon monoxide ratios.

Figure 7. Long time-on-stream for perovskite catalyst calcined at 725 °C, using 0.05 g of catalyst with GHSV of 84 L/g/h; T = 700 °C.
Figure 10 presents the output of the thermogravimetric analysis (TGA) of the used catalysts after 8 h on reaction at 700 °C. The measured weight drop denoted the influence of pressure. The catalyst operated at 1 bar gave 33% weight drop, while the catalysts operated at higher pressures (3 and 5 bar) gave a higher weight loss of about 63%. On the hand, the catalyst operated at 7 bar gave the highest weight loss of 83%. This is justified since the tendency of carbon formation increased with the pressure increase. Figure 11 displays the result of the thermogravimetric analysis (TGA) of the used catalysts for two reaction times (8 h and 30 h) operated on 1 bar pressure and at 700 °C. The measured weight drop compared the influence of time on stream. The catalyst operated for 8 h time on stream gave 33% weight drop, while the catalysts operated for 30 h time on stream produced a 47% weight loss. The 14% increase of the weight drop for the longer time on stream is reasonable as the carbon formation increased with the reaction increase.

The TGA investigation exhibits the influence of operation pressure, where high pressure favors the increase of carbon deposition. Figure 12 exhibited the TPO of the used perovskite catalyst for 1 bar pressure at two different reaction durations (8 h and 30). The TPO tests were accomplished with the used Na0.5La0.5Ni0.3Al0.7O2.5 catalysts operated at 700 °C. The TPO patterns showed the presence of a single peak for each reaction time with maxims at 500 °C and 620 °C for 8 h and 30 h respectively. This showed the increase of the reaction time affected the structure of the carbon deposited and its quantity. The higher reaction time favored the formation of graphitic carbon as its peak was shifted to the higher region temperature. It is remarkable that 1 bar operated for 8 h has its peak appeared at relatively lower temperature and hence more resistant to the surface oxidation than 1 bar operated for 30 h.

Figure 8. Cont.
The identification of the types of carbon deposited over used catalysts in DRM is crucial in comprehending its deactivation behaviour. Thus, temperature programming oxidation (TPO) analysis is often carried out. Figure 9 displayed the TPO of the used perovskite in this work for four different pressures (1, 3, 5, and 7 bar). The TPO tests were performed with spent Na0.5La0.5Ni0.3Al0.7O2.5 catalysts operated at 700 °C and lasted for 8 h of reaction. The TPO patterns demonstrated the presence of a single peak for each pressure with maxims at 500 –620 °C. This can be assigned to polymeric respectively [34]. The type of coke represented here for high pressure was graphic carbon deposited on the support which metallic centre did not catalyse and removed at T > 650 °C [35] and this type of coke can be totally removed using pure O2 at 700 °C. The TPO analysis discloses the formation of amorphous carbon at 1 bar while high pressure forms graphitic carbon. The shifting of peaks toward high temperature denotes the growth tendency of graphitic carbon. The TPO analysis

Figure 8. SEM images of (A) fresh catalyst, (B) used catalyst at 1 bar, (C) used catalyst at 7 bar.
confirms the TGA analysis showing the increase formation of carbon deposit with the increase of pressure.

Figure 9. TPO of the used catalyst, calcined at 725 °C, after 8 h reaction time in DRM at 700 °C.

Figure 10 presents the output of the thermogravimetric analysis (TGA) of the used catalysts after 8 h on reaction at 700 °C. The measured weight drop denoted the influence of pressure. The catalyst operated at 1 bar gave 33% weight drop, while the catalysts operated at higher pressures (3 and 5 bar) gave a higher weight loss of about 63%. On the hand, the catalyst operated at 7 bar gave the highest weight loss of 83%. This is justified since the tendency of carbon formation increased with the pressure increase. Figure 11 displays the result of the thermogravimetric analysis (TGA) of the used catalysts for two reaction times (8 h and 30 h) operated on 1 bar pressure and at 700 °C. The measured weight drop compared the influence of time on stream. The catalyst operated for 8 h time on stream gave 33% weight drop, while the catalysts operated for 30 h time on stream produced a 47% weight loss. The 14% increase of the weight drop for the longer time on stream is reasonable as the carbon formation increased with the reaction increase.

Figure 10. TGA patterns for catalyst, calcined at 725 °C, after 8 h reaction time in DRM, operated at 700 °C for pressure (1, 3, 5, 7 bar); GHSV 84,000 (mL/(g h)).
Figure 11. TGA patterns for catalysts, calcined at 725 °C, after 8 h and 30 h reaction times in DRM, operated at 700 °C for 1 bar pressure; GHSV 84,000 (mL/(g h)).

Figure 12. TPO of the used catalysts, calcined at 725 °C for different reaction time in DRM at 700 °C; 1 bar.

Catalysts 2019, 9, x FOR PEER REVIEW 13 of 18 bar pressure at two different reaction durations (8 h and 30). The TPO tests were accomplished with the used Na0.5La0.5Ni0.3Al0.7O2.5 catalysts operated at 700 °C. The TPO patterns showed the presence of a single peak for each reaction time with maxima at 500 °C and 620 °C for 8 h and 30 h respectively. This showed the increase of the reaction time affected the structure of the carbon deposited and its quantity. The higher reaction time favored the formation of graphitic carbon as its peak was shifted to the higher region temperature. It is remarkable that 1 bar operated for 8 h has its peak appeared at relatively lower temperature and hence more resistant to the surface oxidation than 1 bar operated for 30 h.

The carbon deposition is a significant feature, which affects the catalytic performance on methane dry reforming reaction. The different carbon type generates different influence on catalytic performance. Thus, Raman spectroscopic analysis was carried out to study the structure of formed carbon over the used catalysts. The attained Raman spectra are shown in Figure 13. For all the used samples, two main spectra were observed at approximately 1470 cm⁻¹ and 1533 cm⁻¹ corresponding to the D (assigned to sp³ hybridized amorphous carbon) and G band (indicated the presence of graphitized carbon), respectively [36]. The G band can be ascribed to the ideal vibration of the graphite layers as a result of the in-plane carbon-carbon stretching. The D band is credited to the structural defect of graphite [37]. In addition, a small shoulder that appeared at 1582 cm⁻¹ can be associated to disordered carbons at the edge [38]. In general, the ratio of the intensity of D band to G band (ID/IG) delivers a measure of the crystalline order of graphite in carbonaceous materials [39]. This indicates that the degree of graphitization is higher for small values of ID/IG. The ID/IG of all the used catalysts exhibited in Figure 13 denotes that the carbon deposits over the catalysts have almost equal disordered amorphous and graphitic structures. The Raman investigation labels similar degree of graphitization regardless of the operating pressure. However, the intensity of the peaks changes with the operating pressure.
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![Figure 13. Room temperature Raman spectra of used catalysts upon 532 nm excitation.](image)

3. Materials

3.1. Catalyst Preparation

The description of the experimental procedure can be partly obtained from our paper [40] and partly from the given support information. Perovskite catalysts have been prepared using a sol–gel technique [41].

The materials used in this work were obtained from Sigma-Aldrich Ltd. with a purity >99%. These include CH\(_3\)CH\(_2\)COOH acid and precursor reagents, La(NO\(_3\))\(_3\)·6H\(_2\)O, Al(NO\(_3\))\(_3\)·9H\(_2\)O, Ni(NO\(_3\))\(_2\)·6H\(_2\)O, and NaNO\(_3\). The chemicals of the precursor were individually mixed with a slight volume of a pre-heated CH\(_3\)CH\(_2\)COOH at 1 bar and 90 °C. Subsequent to dissolution, every solution was well stirred at 1 bar at 130 °C for 2 h. Subsequently, a reflux process was used to distil the acid
until a gel was seen. The gel was dried at 90 °C overnight and then calcined in air at 725 °C for 4 h. The formula of the obtained catalyst was Na_{0.5}La_{0.5}Ni_{0.3}Al_{0.7}O_{2.5} [35,42].

3.2. Catalyst Performance

DRM was accomplished in a tubular reactor (ID = 0.9 cm) at 1 bar. The reactor was obtained from PID Eng. & Tech. In the event of carrying out the DRM test, a 50 mg catalyst was reduced with 20 mL/min of hydrogen at 750 °C for 1 h. Nitrogen was passed to the reactor for 0.33 h to desorb the attached H\textsubscript{2} meanwhile, the reaction temperatures (500–800 °C) move to the desired values. Similarly, the pressure varied from (1–7 bar).

Later on, CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2} were introduced at the rates of 1800, 1800, and 60 mL/h, in that order. A GC (GC-2014 SHIMADZU) equipped with a thermal conductivity detector and Porapak Q and Molecular Sieve 5A columns, was linked in bypass/series attachments to get the entire constituents of the effluent gas stream. The formulas for conversion and yield are

\[
\%CH_4\text{ conversion} = \frac{CH_4\text{ in} - CH_4\text{ out}}{CH_4\text{ in}} \times 100
\]

\[
\%CO_2\text{ conversion} = \frac{CO_2\text{ in} - CO_2\text{ out}}{CO_2\text{ in}} \times 100
\]

\[
\text{H}_2\text{ Yield (\%)} = \frac{\text{moles of H}_2\text{ produced}}{X \times \text{moles of CH}_4\text{ in the feed}} \times 100
\]

\[
\text{CO Yield (\%)} = \frac{\text{moles of CO produced}}{X \times (\text{moles of CH}_4\text{ in the feed})} \times 100
\]

\[
\text{Deactivation Factor (\%DF)} = \frac{\text{Final Conversion of CH}_4 - \text{Initial conversion of CH}_4}{\text{Initial conversion of CH}_4} \times 100
\]

3.3. Catalyst Characterization

The N\textsubscript{2}-physisorption was used to compute the specific surface area using a Micromeritics Tristar II (Micromeritics, Atlanta, GA, USA). The analysis was achieved by N\textsubscript{2} adsorption-desorption accomplished at −196 °C. Prior to the analysis, each sample was degassed at 200 °C for 3 h. in the flow of nitrogen gas.

The determination of TPR was carried out by means of Micromeritics AutoChem II apparatus (Micromeritics, Atlanta, GA, USA). A 0.7 g catalyst was put in the TPR compartment and flowed with Ar at 150 °C for 0.5 h. After that the temperature was decreased to the ambient temperature. Eventually, at 10 °C/min ramp, the furnace temperature was raised to 1000 °C while the H\textsubscript{2}/Ar mixture was kept at 0.04 L/min. A thermal conductivity detector (TCD) was employed to monitor the signals denoting the hydrogen utilization.

The (CO\textsubscript{2}-TPD) measurement was carried out using Micromeritics AutoChem II (Micromeritics, Atlanta, GA, USA). A 0.5 g of catalyst was activated with H\textsubscript{2} at 600 °C for 60 min. under He (30 mL/min), after that reduced the temperature to 50 °C. The flow rate of CO\textsubscript{2} was maintained for an hour, and He gas was used to expel any physisorbed CO\textsubscript{2}. The desorption figure outline of the catalysts was registered by raising the temperature up to 800 °C at the rate of 10 °C/min. The CO\textsubscript{2} composition in the outflow stream was determined by a thermal conductivity detector. The desorbed CO\textsubscript{2} quantities during TPD were calculated from the areas under the peaks.

The (TPO) was done in O\textsubscript{2} ambient to find out the type of carbon formed on the surface of the catalyst via Micromeritics AutoChem II (Micromeritics, Atlanta, GA, USA). A 0.5 g of sample was activated with H\textsubscript{2} at 600 °C for 60 min. under He (30 mL/min), after that reduced the temperature to 50 °C. The flow rate of CO\textsubscript{2} was maintained for an hour, and He gas was used to expel any physisorbed CO\textsubscript{2}. The desorption figure outline of the catalysts was registered by raising the temperature up to 800 °C at the rate of 10 °C/min. The CO\textsubscript{2} composition in the outflow stream was determined by a thermal conductivity detector. The desorbed CO\textsubscript{2} quantities during TPD were calculated from the areas under the peaks.

TGA was used to determine the carbon formed on the surface of the used catalyst under air by a Shimadzu TGA-15 SHIMADZU analyzer (Shimadzu Corporation, Kyoto, OP, Japan). The temperature
of spent catalyst (0.10–0.15 g) was raised to 1000 °C at the rate of 20 °C/min and the weight loss was determined.

XRD was used for phase identification of catalysts, with Cu Kα radiation functioned at 40 kV and 40 mA. A 0.01° scanning step and 10°–85° range of 2θ were adopted.

The scanning electron microscopy (SEM) was used to examine the surface structure of the catalysts. The images of the fresh and used catalysts were provided by JSM-7500F (Rigaku Corporation, Dover, DE, USA).

4. Conclusions

As a summary, perovskite catalyst employed for CO2 reforming of CH4 was examined in this work. The catalytic performance of methane dry reforming could be greatly influenced by the operating pressure and temperature. Catalysts operated at 1 bar pressure gave the best catalytic and stability performance. The rise of reaction temperature from 500 to 800 °C increases the activity. The H2/CO ratio acquired approximately a unity ratio in operating at 1 bar pressure for temperatures at 600 °C and beyond. Correspondingly, the time on stream tests showed that the best ratio close to unity with a stable profile can be achieved operating at 1 bar pressure. The TPO analysis gave single peaks around 600–650 °C symbolizing the graphitic type of coke which can be eliminated using pure O2 and operating at 700 °C. While the TGA analysis indicated that higher pressure operations favor greater amounts of coke formation. The characterizations of the Raman, EDX, TGA, and TPO all presented the formation of carbon.

Author Contributions: A.S.A.-F., A.A.I., and S.O.K. synthesized the catalysts, carried out all the experiments and characterization tests, and wrote the manuscript. J.K.A.-D. prepared the catalyst and contributed in proofreading of the manuscript. A.E.A. and A.H.F. contributed to the analysis of the data and proofread the manuscript. All authors have read and agreed to the published version of the manuscript.

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