Dry Reforming of Methane Using Ni Catalyst Supported on ZrO$_2$: The Effect of Different Sources of Zirconia

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Abstract: Dry reforming of methane (DRM) has a substantial potential to provide a cost-effective process and in reducing greenhouse gases. Its application has been hindered by carbon deposition and instability problems. The use of an appropriate catalyst is influenced by the support type. The objective of this investigation is to elucidate the effect of different sources of ZrO$_2$ support. Four kinds of ZrO$_2$, namely RC-100 and Z-3215, MKnano, and ELTN were acquired from Japan, Canada, and China, respectively. The catalyst samples were analyzed by BET, XRD, TPR, TPD, TEM, TGA, TPO, FT-IR, and Raman. The analysis of the structural properties displayed that all Ni-supported catalysts, regardless of their source, are mesoporous and that 5Ni-RC-100 possessed the highest BET surface area of 17.7 m$^2$/g and 5Ni-MKnano had the lowest value of BET 3.16 m$^2$/g. In the TPD and TEM analysis, the 5Ni-RC-100 catalyst presented the highest intensity of basicity and the minimum average particle size of 3.35 nm, respectively. The 5Ni-RC-100 catalyst outperformed 5Ni-ELTN by exhibiting 44% higher CH$_4$ conversion; however, 5Ni-RC-100 gave the highest weight loss in the TGA analysis of 66%.

Keywords: coke; CO$_2$ reforming of CH$_4$; different sources of zirconia support; Ni catalyst

1. Introduction
The CH$_4$ reforming with CO$_2$ has attained wide interest in the recent era because the process utilizes greenhouse gases that cause global warming [1–3]. The Equation (1) reaction is heat-absorbing (ΔH° = 247 kJ/mol) and entails high reaction temperature that prompts numerous side reactions:

$$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2 \quad (1)$$

$$\text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2 \rightarrow \text{CH}_4 \text{ decomposition} \quad (2)$$

$$2\text{CO} \leftrightarrow \text{C} + \text{CO}_2 \rightarrow \text{Boudouard reaction} \quad (3)$$

$$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \rightarrow \text{reverse water-gas shift} \quad (4)$$

The reforming reaction results from the scission of CH$_4$ due to the heating process, followed by gasification of the formed carbon by CO$_2$ adsorption on the support. This process is not presently industrialized due to the drastic carbonization and agglomeration of the catalysts in the high-temperature reaction [4]. Hence, it is indispensable to look for an effective catalyst to prevent the agglomeration and carbon deposition to accomplish promising performances in the process. Noble metals, which are extremely active and stable in the reforming process of CH$_4$, are preferably avoided, owing to their inadequate availability and high price [5–6]. Transitional metals, particularly Ni-based catalysts have been explored largely owing to the high activity performance of Ni and its cheap
price [9–12]. Nevertheless, the Ni metal is susceptible to carbon formation resulting from methane breakdown [13], which is mainly influenced by the Ni particle diameter and is preferred in big Ni sizes. To reduce this effect, often porosity and/or the metal particles are embedded in the oxide matrix [14–16]. Moreover, the type of support can also have a crucial part in adjusting the size of Ni particles. Catalytic supports could also play a significant part in the catalytic performance of the catalyst. Diverse catalytic reactions comprising the reactants, intermediates, and products could occur at different surface sites of support oxides. It is vastly understood that supports and active metal coordination are vital for the efficiency of the catalysts. Because of the active metal bonding and support, the support types can considerably modify the reactivity of the metal element [17]. In the area of catalysis, supports contribute to the lifespan and stability of the catalysts. Researchers have acknowledged that the creation of carbon on Ni-based catalysts are affected by the acidity and basicity of the support. For instance, supports like Al$_2$O$_3$ intensify the acidity of catalysts [18]. The breaking down of CH$_4$ that yields carbon is enhanced by supports that are acidic [17]. Alternatively, it was established that basic supports play an important part in the efficiency of catalysts by adjusting Lewis acidity and therefore the coking [19]. In addition, supports that furnish O$_2$ may enhance the oxidation of the coke over the metal. The splitting of CO$_2$ on the surface is improved by oxygen vacancies [20]. The stability of the catalyst is dictated by the correspondence between the degree of CH$_4$ breakdown and the level of carbon removal [21]. A remarkable metal-support interaction is manifested by the Ni supported on ZrO$_2$. Thus, zirconia-based supports have been inspected, mainly since zirconia presents considerable ionic conductivity owing to its promptness to create defects and oxygen vacancies, plus high thermal stability. The employment of a stable support like zirconia promotes oxygen vacancy and stability of Ni-formed catalysts [22]. In addition to its high Lewis basicity, ZrO$_2$ is also branded by high resistance and its firm crystallinity over an extensive range of working temperatures.

In this paper, a comparative study of different sources of zirconia-supported Ni catalysts, on the catalytic activity and stability in the CO$_2$ reforming of methane was studied. The wet impregnation method was adopted for catalyst preparation. The fresh and used catalysts were characterized by XRD, BET, TPR, TPD, TGA, TEM, TPO, and FTIR to display the source influence on ZrO$_2$ support upon the efficiency of the dry reforming of CH$_4$.

2. Results and Discussions
2.1. Characterization

Figure S1 illustrates the N$_2$ adsorption-desorption tests for Ni supported on ZrO$_2$ obtained from different ZrO$_2$ sources to explicate the mesopores of the catalysts. The pore volume, pore size, and BET surface areas of the different ZrO$_2$ sources-supported Ni are illustrated in Table 1. In the table, N$_2$ adsorption-desorption isotherms of the different ZrO$_2$ sources supported are seen. The Ni catalyst displays a typical type V isotherm. The hysteresis loop of the graph is H3-type, in which the adsorption branch resembles a Type II isotherm [23,24]. The initial location of the isotherm is attributed to the relatively weak adsorbent–adsorbate interactions. At higher P/Po, molecular clustering is followed by pore filling, and therefore the H3 type of hysteresis loop was spotted when P/Po was in the range of 0.85 to 1.0. This determines that catalysts are mesoporous. The 5Ni-MKnano catalyst exhibited the lowest quantity adsorbed (0.77 mmol/g), while 5Ni-ELTN presented the highest quantity adsorbed (4.5 mmol/g). It can be realized that the surface area of the 5Ni-RC-100, 5Ni-ELTN, 5Ni-Z-3215, and 5Ni-NKnano catalysts are 17.70 m$^2$/g, 15.51 m$^2$/g, 9.81 m$^2$/g, and 3.16 m$^2$/g, respectively. Normally, higher surface area and pore volume offer higher catalytic activity since reactant adsorption upon the catalyst and metal dispersion are improved. Therefore, 5Ni-RC-100 and 5Ni-ELTN, are preferable over 5Ni-Z-3215 and 5Ni-MKnano.

In Figure S2, the BJH adsorption cumulative pore volume model was hence used for the adsorption branch of the isotherms to compute pore size distribution. All types of
supports indicated pore volume rise along with the pore size when the diameter is below 100 nm. The 5Ni-Z-3215 and 5Ni-Maknano catalysts assumed the lowest pore volume, whereas the 5Ni-ELTN had the highest pore volume.

Table 1. Textural properties of Ni catalysts supported on various ZrO$_2$ sources: BET specific surface area ($S_{BET}$), pore volume ($V_p$), and pore width ($D_p$).

| Catalysts  | $S_{BET}$ (m$^2$/g) | $V_p$ (cm$^3$/g) | $D_p$ (nm) |
|------------|---------------------|------------------|------------|
| 5Ni-RC-100 | 17.7                | 0.12             | 31.7       |
| 5Ni-ELTN   | 15.5                | 0.13             | 38.6       |
| 5Ni-Z-3215 | 9.8                 | 0.05             | 24.8       |
| 5Ni-MKnano | 3.2                 | 0.02             | 4.1        |

The analysis of x-ray diffraction of fresh catalysts was achieved to find their crystallinity and structure. The peaks of fresh catalysts are displayed in Figure 1. As presented, the Ni diffraction lines were evidently spotted at two theta values of 37.5° and 42.2° of fresh samples. While the peaks at 17.2°, 24.1°, 28.2°, 31.4°, 34.1°, 35.1°, 40.8°, 48.4°, 50.0°, 55.5°, 57.5°, 59.8°, and 62.6° were assigned to the monoclinic ZrO$_2$ (JCPDS file no. 81-1314). On the other hands, the tetragonal ZrO$_2$ diffraction peaks are situated at 29.8°, 34.2°, 35.1°, 50.0°, and 59.8° [25]. The reducibility aspects of the Ni catalysts supported on different ZrO$_2$ sources were investigated using the hydrogen temperature programming reduction technique. The reduction peaks exhibited are credited to NiO reduction to Ni°. Similar results were reported by other investigators [26–28]. They found that the low-temperature peak is ascribed to the highly dispersed surface NiO species and the high-temperature peak is ascribed to the bulk NiO, with no reduction peak for ZrO$_2$ support.

![XRD of different sources of zirconia-supported Ni samples.](image)

Figure 1. XRD of different sources of zirconia-supported Ni samples.

Temperature-programmed reduction profiles are plotted in Figure 2, where all samples displayed similar numbers of peaks in the range of 100–850 °C. In the moderately low temperature, all the samples revealed two peaks, except the 5Ni-MKnano, which showed wide and shoulder peaks at 400 °C and 725 °C, respectively. The less intensity reduction peaks centered at 270–340 °C were credited to the free nickel oxide that is not bound to the support, whereas the broad higher intensity peaks centered at 433–508 °C were associated with the NiO moderately attached to the support and dispersed well in the zirconia.
The activity of the catalysts is influenced by the extent of $H_2$ consumed and the level of NiO attached to the support. The 5Ni-RC-100 and 5Ni-Z-3215 assume quantities of $H_2$ consumed below 600 $\mu$mol/g at 340–500 °C, while 5Ni-Mknano and 5Ni-ELTN get quantities of $H_2$ consumed higher than 600 $\mu$mol/g. This demonstrates that the higher activity of the catalyst is dependent on the balanced amount of interaction between the active metal and support and partly justifies the lower activity of 5Ni-Mknano and 5Ni-ELTN.

The shoulder peak of 5Ni-MKnano was related to the firm interplay of the nickel and support. The 5Ni-MKnano catalyst possessed the highest total quantity consumed of hydrogen, as shown in Table 2. Table 2 indicated the total reduction of catalysts and dispersion. The calculations of the degree of reduction and dispersion of Ni are described in Supplementary Information. It is known that metal dispersion and particle width are two factors that are essential for the development of catalysts with enhanced activity and stability. The extent to which an active metal is uniformly scattered over the existing surface area of a support is a good index of catalyst stability [29,30]. The peaks of 5Ni-RC-100, 5Ni-ELTN, and 5Ni-Z-3215 catalysts have intensities of 0.02, 0.02, and 0.02 (a.u.), respectively. These peaks have displayed relatively low intensities. On the other hand, the higher temperature peaks have intensities of 0.04, 0.04, 0.06, and 0.07 (a.u.) respectively, for 5Ni-Z-3215, 5Ni-MKnano, 5Ni-RC-100, and 5Ni-ELTN (a.u.), denoting that 5Ni-RC-100 and 5Ni-ELTN have better NiO synergy with the support.

Table 2. The analysis of $H_2$ consumption during $H_2$-TPR.

| Samples       | Temperature (°C) | Quantity Consumed ($\mu$mol/g) | Exp. Total ($\mu$mol/g) | Reduction % | Dispersion % |
|---------------|------------------|--------------------------------|-------------------------|-------------|--------------|
| 5Ni-RC-100    | 282.5            | 42.1                           | 576.9                   | 68          | 0.39         |
|               | 463.0            | 534.8                          |                         |             |              |
| 5Ni-ELTN      | 275.4            | 54.0                           | 624.1                   | 73          | 0.55         |
|               | 443.6            | 570.1                          |                         |             |              |
| 5Ni-Z-3215    | 284.3            | 129.0                          | 742                     | 87          | 0.58         |
|               | 411.6            | 582.1                          |                         |             |              |
|               | 752.5            | 30.9                           |                         |             |              |
| 5Ni-MKnano    | 327.8            | 305.4                          |                         |             |              |
|               | 404.9            | 450.0                          | 805.6                   | 94          | 0.14         |
|               | 714.8            | 50.2                           |                         |             |              |
The CO$_2$-TPD analysis was performed for different sources of ZrO$_2$ supported on Ni samples to describe the basic sites and the entire basicity of the sample. It has been normally understood that basic supports like ZrO$_2$ facilitate the separative adsorption of carbon dioxide, which can bring about the inhibition of coke by generating a greater quantity of oxygen atoms close to the catalytic active metal surface [31,32]. Therefore, the improvements of basic sites by using ZrO$_2$ affected the decrease of carbon formation [33,34]. However, excessive amounts of CO$_2$ dissociation on the catalyst surfaces via boosting basicity could make the catalyst inactive. Alternatively, excessive surface basicity makes catalyst inactive via coking [35]. Therefore, the extent of the basicity of catalysts should be balanced to secure the good performance of the catalyst. Figure 3 displays the desorption profiles and CO$_2$ uptake data of Ni catalysts supported on different ZrO$_2$ sources.

The zirconia-support structure owned hydroxyl (OH$^-$) [36] could be formed from metal coordination during the synthesis, therefore, hydrogen carbonate was formed from the reaction between the OH$^-$ group with CO$_2$ molecules [37]. The weak basic site was spotted at 100 °C, while the moderate basic site was spotted at 300 °C, as established earlier in the characterizations concerning the basicity of the Ni sample [38]. The catalysts 5Ni-RC-100 and 5Ni-Z-3215 presented the highest quantity of basicity, while the 5Ni-MKnano and 5N-ELTN catalysts assumed the lower quantities of basicity, as depicted in the analysis of CO$_2$ consumption during TPD of Table S1, and therefore the catalytic reactivity of catalysts is enhanced by the quantity of the basic sites. The FT-IR spectroscopy of the calcined Ni/ZrO$_2$ catalysts was investigated to identify types of bonds. The IR spectra of Figure 4 showed transmissions bands centered at 549–587 and 612 cm$^{-1}$ typical for Ni-O and Zr-O stretching vibrations [39]. The band at 722–724 cm$^{-1}$ can be attributed to the ZrO$_2$.

TEM analysis of the fresh nickel catalysts supported upon different ZrO$_2$ sources is displayed in Figure 5. Figure 5A clearly demonstrates the TEM images of fresh Ni-ZrO$_2$. The Ni particles are well scattered. The spread of the atoms is visible displaying the non-existence of support-interaction partly, as depicted in the TPR evaluation. The effect of this little support-metal synergy makes the nickel particles wander spontaneously on the surface of the catalyst, where they unite other particles and increase the size by a diffusive effect. Figure 5B displays the fresh catalyst particle size distribution with a particle mean diameter of 3.35 nm.

![Figure 3. CO$_2$ TPD profiles of different ZrO$_2$ sources supported Ni samples.](image-url)
Figure 3. CO2- TPD profiles of different ZrO2 sources supported Ni samples.

Figure 4. Comparison of FT-IR spectra of Ni catalysts supported on different sources of zirconia.

2.2. Results of Activity

The catalytic results of reforming CH4 using Ni catalysts supported on different sources of zirconia- for 420 min of time on-stream (TOS) are shown in Figures 6 and 7. The feed was kept constant at 42,000 mL/h/g_cat. The reaction was accomplished at 700 °C, 1 atom. The results exhibited the impact of different sources of zirconia supports. It is clear that the source had a substantial impact on the activity and stability of CO2 reforming of methane. In Figure 6, the 5Ni-RC-100 catalyst exhibited the highest initial CH4 conversion of 67.4% and an average conversion of 53.5%, In contrast, the 5Ni-ELTN catalyst displayed the lowest initial CH4 conversion of 42.3% and an average conversion of 34.9%. The pronounced catalytic activity of the 5Ni-RC-100 sample could be generally associated with the high BET surface area shown in Table 1, which resulted from the appropriate interplay with the supports, as displayed in the XRD and TPR. Moreover, the high performance of the 5Ni-RC-100 sample is predictable as the BET results indicated that it had the greatest specific surface area. It was reported that higher surface area and pore volume usually improve catalyst activity [40]. Figure 7 presents the catalytic results of CH4 reforming in terms of CO2 conversion. It can be seen that the CO2 conversions of all catalysts are higher than their corresponding methane conversion by an average of 10%. This is because of the reverse water gas shift reaction according to Equation (4) [41]. The 5Ni-RC-100 and 5Ni-Z-3215 catalysts gave an initial average CO2 conversion of about 69%, while the 5Ni-MKnano and 5Ni-ELTN provided lower initial average CO2 conversions of about 56.7% and 52.8%, respectively. Table 3 displays the reactant conversions, the calculated deactivation factor, and the coke formed. The 5Ni-RC-100 sample displayed the greatest values of deactivation factor and coke, whereas Table 4 exhibits the activity performance of the present and literature work.
2.2. Results of Activity

The catalytic results of reforming CH₄ using Ni catalysts supported on different sources of zirconia for 420 min of time on-stream (TOS) are shown in Figures 6 and 7. The feed was kept constant at 42,000 mL/h/g cat. The reaction was accomplished at 700 °C, 1 atom. The results exhibited the impact of different sources of zirconia supports. It is clear that the source had a substantial impact on the activity and stability of CO₂ reforming of methane. In Figure 6, the 5Ni-RC-100 catalyst exhibited the highest initial CH₄ conversion of 67.4% and an average conversion of 53.5%. In contrast, the 5Ni-ELTN catalyst displayed the lowest initial CH₄ conversion of 42.3% and an average conversion of 34.9%. The pronounced catalytic activity of the 5Ni-RC-100 sample could be generally associated with the high BET surface area shown in Table 1, which resulted from the appropriate interplay with the supports, as displayed in the XRD and TPR. Moreover, the high performance of the 5Ni-RC-100 sample is predictable as the BET results indicated that it had the greatest specific surface area. It was reported that higher surface area and pore volume usually improve catalyst activity [40]. Figure 7 presents the catalytic results of CH₄ reforming in terms of CO₂ conversion. It can be seen that the CO₂ conversions of all catalysts are higher than their corresponding methane conversion by an average of 10%. This is because of the reverse water gas shift reaction according to Equation (4) [41]. The 5Ni-RC-100 and 5Ni-Z-3215 catalysts gave an initial average CO₂ conversion of about 69%, while the 5Ni-MKnano and 5Ni-ELTN provided lower initial average CO₂ conversions of about 56.7% and 52.8%, respectively. Table 3 displays the reactant conversions, the calculated deactivation factor, and the coke formed. The 5Ni-RC-100 sample displayed the greatest values of deactivation factor and coke, whereas Table 4 exhibits the activity performance of the present and literature work.

Figure 5. TEM images and matching particle size distribution for fresh: (A,B) 5Ni-RC100, (C,D) 5Ni-ELTN, (E,F) 5Ni-Z-3215, and (G,H) 5Ni-MKnano catalysts calcined at 700 °C.
Figure 6. CH$_4$ conversion for different source zirconia-supported Ni catalysts.

Figure 7. CO$_2$ conversion for different source zirconia-supported Ni catalysts.
Table 3. Conversions of CH\textsubscript{4} and CO\textsubscript{2}, deactivation factor, coke formed.

| Samples      | Initial CH\textsubscript{4} Conv. (%) | Final CH\textsubscript{4} Conv. (%) | Initial CO\textsubscript{2} Conv. (%) | Final CO\textsubscript{2} Conv. (%) | DF (%) | Coke %wt. Loss |
|--------------|--------------------------------------|-------------------------------------|---------------------------------------|-------------------------------------|--------|----------------|
| 5Ni-RC-100   | 67.4                                 | 46.5                                | 68.4                                  | 58.2                                | 31     | 66.3           |
| 5Ni-ELTN     | 42.3                                 | 31.9                                | 52.3                                  | 43.9                                | 27     | 25.2           |
| 5Ni-Z-3215   | 62.2                                 | 45.3                                | 69.5                                  | 58.4                                | 24     | 38.3           |
| 5Ni-MKnano   | 51.2                                 | 36.3                                | 56.7                                  | 46.4                                | 29     | 46.9           |

DF (%) = \(\text{Initial methane conversion} - \text{Final methane conversion})/\text{Initial methane conversion} \times 100; Coke = obtained from TGA.

Table 4. CH\textsubscript{4} conversion obtained and those in the past employing various supports of Ni catalysts for CO\textsubscript{2} reforming of CH\textsubscript{4}.

| Reference | Sample                  | CH\textsubscript{4}:CO\textsubscript{2} | %CH\textsubscript{4} Conv. | WHSV | T °C |
|-----------|-------------------------|----------------------------------------|-----------------------------|------|------|
| [9]       | Ni-Al\textsubscript{2}O\textsubscript{3} 1:1 | 36                                      | 6000                        | 800  |
| [42]      | Ni-SiO\textsubscript{2} 1:1 | 50                                      | 48,000                      | 800  |
| [43]      | Ni-H-ZSM-5 1:1          | 76                                      | 3600                        | 700  |
| [44]      | Ni-MgO 1:1              | 70                                      | 86,000                      | 760  |
| This work | Ni-ZrO\textsubscript{2} (RC-100) 1:1 | 54                                      | 42,000                      | 700  |

Figure 8 illustrates the Raman spectra of the spent catalysts. The spectra can be categorized into two zones. Zone I extends from 1200 and 1600 cm\textsuperscript{-1}, where two distinct peaks appeared as “D-band and G-band”. The D-band centers about 1341 cm\textsuperscript{-1} and designates the imperfections owing to a disorder [40], whereas G-band is attributable to graphite centers around 1577 cm\textsuperscript{-1}. The G band results from the vibration of neighboring carbon atoms. Zone II extends between 2500 and 2800 cm\textsuperscript{-1}. A peak is displayed at around 2683 cm\textsuperscript{-1}; it is for 2D, developed from the combinations and associates with the bands of zone I [40]. The proportional intensity (I\textsubscript{D}/I\textsubscript{G}) could be related to carbon crystallinity. The decimal numbers obtained signify the tendency to crystalline caused by graphitic carbon. The I\textsubscript{D}/I\textsubscript{G} ratios are 0.87, 0.92, 0.92, and 0.50 for the 5Ni–RC-100, 5Ni–ELTN, 5Ni–Z-3215, and 5Ni–MKnano, respectively. The Raman results predict the presence of a small quantity of graphitic carbon.

![Figure 8. Raman spectra of used different sources of zirconia-supported Ni catalysts operated at 700 °C for 7 h.](image-url)
TGA, a quantitative analytic technique was accomplished on the spent catalysts to compute the quantity of carbon formed on the catalysts. The spent catalysts were obtained as a result of a dry reforming reaction at 700 °C after a duration of 420 min. Figure 9 depicts the extent of carbon formed with respect to the % weight drop of Ni catalysts supported on different ZrO$_2$ sources. The mass reduction for all the catalysts began at the range near 500–550 °C. The plots depict that the 5Ni-RC-100 sample has the greatest quantity of carbon formation with a 66.3% weight drop. This was likely as the catalyst had the biggest deactivation factor of about 31%, while the 5Ni-ELTN catalyst had the lowest value of carbon formation of about 25.2% weight drop. The TPO analysis determines the type and carbon amount of used catalysts. It is shown in Figure 10. Many investigators have reported that carbon deposits can be regarded as amorphous, filamentous, graphitic carbon, and bulk carbon [45,46]. The amorphous carbon is the most active, being consumed rapidly by the Boudard reaction (Equation (3)). Filamentous and graphitic carbons not only obstruct active sites but are also removed at a lower rate than amorphous carbon. Bulk carbon generates speedy inactivity covering the active sites and that this carbon is not used during the Boudard reaction. Figure 10 exhibits the TPO analysis of the spent catalysts using Ni supported on different sources of zirconia. It appears that all samples were gasified between 300 and 647 °C, indicating the dominance of amorphous carbon formation. Besides, the appearance of broad peaks in the curves is due to the slow-burning carbon deposited. The 5Ni-RC-100 sample presented the highest intensity of CO$_2$ formation rate, while the 5Ni-ELTN sample gave the lowest. The TPO result is coherent with that of the Raman and TGA.

![TGA profile of different ZrO$_2$ sources supported Ni catalysts.](image-url)
Figure 9. TGA profile of different ZrO\textsubscript{2} sources supported Ni catalysts.

Figure 10. TPO analysis of the used catalysts.

3. Experimental

3.1. Materials

Hydrated Ni nitrate, 98\%, was procured from Riedel-De Haen AG, Seelze, Germany. The zirconia supports, RC-100 and Z-3215, MKnano, and ELTN were acquired from Osaka, Japan, Mississauga, Canada, and Anhui, China, respectively. The detailed sources of the supports are given in Supplementary Information.

3.2. Catalyst Formation

The method of wet-impregnation was used for the desired catalyst development; the adopted procedure is given in Supplementary Information and in our previous work [47].

3.3. Characterization

The feature of the catalysts was accomplished in accordance with the procedure and stated in Supplementary Information.

3.4. Catalytic Activity

The CO\textsubscript{2} reforming CH\textsubscript{4} reactions were performed in a fixed bed (0.91 cm diameter and 13.00 cm long) at 1 atm. The PID Eng. & Tech Microactivity Reference Company (Madrid, Spain) provided the reactor. H\textsubscript{2} flow of 1,200 L/h for an hour at 700 °C was used to reduce 0.1 g of the catalyst. Then, the bed was injected with N\textsubscript{2} for a quarter of an hour to remove the physically adsorbed H\textsubscript{2}. In each test, N\textsubscript{2}/CO\textsubscript{2}/CH\textsubscript{4} gas ratios of 1:3:3, respectively, were used in the rate at 4.2 L/h. A GC-2014 (Shimadzu Corporation, Kyoto, OP, Japan) analyzed the gas compositions. The reproducibility was maintained considering the average value of three runs. The catalysts were then removed from the reactor for characterization. The conversions of CH\textsubscript{4} and CO\textsubscript{2} were expressed as:

\[
\text{%CO}_2 \text{ conversion} = \frac{(CO_2)_{in} - (CO_2)_{out}}{(CO_2)_{in}} \quad (5)
\]

\[
\text{%CH}_4 \text{ conversion} = \frac{(CH_4)_{in} - (CH_4)_{out}}{(CH_4)_{in}} \quad (6)
\]
4. Conclusions

In this work, Ni samples supported on different sources of zirconia were employed for CO$_2$ reforming of methane. The zirconia supports, RC-100 and Z-3215, Mknano, ELTN were obtained from Japan, Canada, and China, respectively. The method of impregnation was adopted to develop the desired catalysts. The reactions were performed in a fixed bed for 7 h period at 700 °C. The source type of zirconia support determined the catalytic efficiency of the process. The 5Ni-RC-100 supported catalyst gave the highest catalytic performance. The TPR analysis gave two prominent peaks before 600 °C, denoting that an appropriate temperature of activation and calcination were used for the different zirconia support types. TGA examination pointed out that the higher conversions promoted larger amounts of carbon deposition. Various kinds of characterization skills were conducted to get a deep understanding of the effect of the sources of ZrO$_2$. The catalyst supported by the RC-100 gave the highest BET surface area, the highest intensity in the TPD analysis, and the lowest particle diameter according to TEM. As expected from the characterization analysis, the RC-100 ZrO$_2$ supported catalyst attained considerably higher conversions of CO$_2$ and CH$_4$, compared to other sources supported catalysts at 700 °C. Alternatively, the 5Ni-ELTN catalyst revealed the least CO$_2$ and CH$_4$ conversions. Therefore, based on the result of the present work, it is recommended to use RC-100 ZrO$_2$ support for dry reforming reaction under similar operating conditions. This catalyst can further improve its stability and activity performance by adding support modifiers and/or catalyst promoters to alleviate carbon deposition.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11070827/s1, Figure S1: N$_2$ adsorption and desorption isotherms; Figure S2: Pore volume versus pore diameter of different ZrO$_2$ sources supported Ni catalysts; Table S1: The analysis of CO$_2$ consumption during TPD.

Author Contributions: A.A.I. and A.S.A.-F., composing of catalysts, writing—original manuscript; A.E.A. and A.H.F. participated in the analysis of the data and proofread the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: National Plan for Science, Technology and Innovation (MAARIFAH), King Abdulaziz City for Science and Technology, Kingdom of Saudi Arabia, Award No. (13-PET1056-02).

Acknowledgments: The authors extend their appreciation to the National Plan for Science, Technology and Innovation (MAARIFAH), King Abdulaziz City for Science and Technology, Kingdom of Saudi Arabia, Award No. (13-PET1056-02).

Conflicts of Interest: The authors declare that they have no competing interest.

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