Effects of Platinum and Palladium Metals on Ni/Mg\textsubscript{1-x}Zr\textsubscript{x}O Catalysts in the CO\textsubscript{2} Reforming of Methane

Faris A. J. Al-Doghachi

Department of Chemistry, Faculty of Science, University of Basra, Basra, Iraq


1. Introduction

Alternative energy resources are highly demanded because the reserves of fossil fuels are depleting very rapidly. Consequently, the use of greenhouse gases, such as CH\textsubscript{4} and CO\textsubscript{2}, as an alternative energy source has gained more importance. The search for methane has ended with favorable results. Methane is readily available, and reserves that are bigger than crude oil reserves have been revealed. CH\textsubscript{4} can be obtained from shale gas and fermented wastes [1]. It is transformed into syngas (a mixture of CO and H\textsubscript{2}), which can be produced through the use of steam, partial oxidation, or carbon dioxide in reforming reactions.

The dry-reforming process involves the conversion of CH\textsubscript{4} and CO\textsubscript{2}, which are two of the cheapest and most abundant carbon-containing materials, into synthesis gas (Equation 1). This
reaction also has very important environmental implications because both methane and carbon dioxide are greenhouse gases, which may be converted into valuable product such as hydrogen. Further, due to its large heat of reaction and reversibility, this process has potential thermo-chemical heat-pipe applications for the recovery, storage, and transmission of solar and other renewable energy sources.

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298}^o = 247.0 \text{ kJ/mol} \ (1) \]

This synthesized gas has become an important raw material for fuels and/or for producing chemicals for industrial use. In fact, fossil fuel and biomass can undergo conversion into syngas. However, for the purpose of industrial application of syngas, the H2/CO molar ratios must be varied. For example, in the synthesis of methanol [2], the H2/CO ratio required is 2. Meanwhile, under a single step process (H2/CO ratio = 1), dimethyl ether can be synthesized [3,4]. It is worth noting that H2/CO ratio plays a critical role in the process of producing syngas [5].

The reaction between DRM and noble metals, such as Pt, Rh, and Ru, is highly active [6]. Furthermore, these metals resist carbon from being formed more effectively compared with other transition metals [7], since Ni catalysts are more favorable with noble metals, such as Rh, Pt, Pd, or Ru. They increase the reaction of the catalysts, and they are more stable in their reaction against coke deposition when compared with that of the other non-favorable Ni catalysts [8]. For instance, bimetallic Ni-Pt that supports ZrO2 shows that it is able to sustain a longer duration of activity time than monometallic Ni/ZrO2. Thus, Ni-Pt catalyst has high potential for industrial application for DRM [9]. The activity and stability of trimetallic Pt-Pd-Ni catalysts are higher than those of the monometallic Ni catalyst [10]. These findings support the idea that Pt-Pd can be used in the prevention of the oxidation of Ni. In a research work on the use of favorable catalysts of Ni/MgO with Ce(III), the findings revealed more active catalytic activity and higher stability for Co-promoted catalysts. This result is supported by Ce-promoted catalysts, in which the resistance of coke deposition was high. As the catalytic activity of Ce-promoted catalysts increases because of their high affinity for oxygen species, the characteristics of the resistance of coke improve. Ce-promoted catalysts exhibited no favorable catalytic performance. The cause for the unfavorable catalytic activity in Ce-promoted catalyst is the segregation of Ce as CeO2. This reaction occurred because of immiscibility with MgO that caused the increase of the size of Ni particles [11].

The present work describes the synthesis of Pt,Pd,Ni/Mg1-xZrxO catalysts (where x = 0, 0.03, 0.07, and 0.15) containing 1 % of each of Ni, Pd and Pt metals, in order to evaluate their activity, selectivity and stability, as well as their ability to decrease the deposition of carbon on the catalyst during the DRM reaction. The effect of 1.25 % O2 on conversion of methane will be studied. The catalyst used in order to enhance the selectivity and stability in compare with to previous work [12].

### 2. Materials and Method

#### 2.1 Preparation of catalysts

The co-precipitation method was used for the preparation of the catalysts, Mg1-xZrxO (x = 0.00, 0.03, 0.07, and 0.15). The support of MgO and promoter zirconia of ZrO2 was prepared according to a literature method [12] by using a 0.1 M ZrCl4(aq) (Merck; >99.0%), Mg(NO3)2.6H2O (Merck; >99.0%), and 1.0 M K2CO3 (Merck; >99.7%). Table 1 represents the amount used as the precipitant: 1 M K2CO3.

Firstly, the sample was washed in warm water after the filtration of the precipitant. Next, dried the sample at 120 °C for 12 h. After that, the precipitant was pre-calcinated in the air at 500 °C for 5 h to remove CO2. Then, pressed the sample into discs at 600 kg/m2. Finally, the sample was calcined at 1150 °C for 20 h to im-

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Support (MgO) Mg(NO3)2.6H2O (g)</th>
<th>Promoter (ZrO2) ZrCl4 (g)</th>
<th>Total weight of MgO and ZrO2 after calcination (g)</th>
<th>Impregnation of the main catalyst (1% Pt) (1% Pd) (1% Ni) (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/MgO</td>
<td>25.0</td>
<td>0.0</td>
<td>1</td>
<td>0.02 0.029 0.044</td>
</tr>
<tr>
<td>Pt,Pd,Ni/Mg0.99Zr4+0.01O</td>
<td>24.9</td>
<td>1.3</td>
<td>1</td>
<td>0.02 0.029 0.044</td>
</tr>
<tr>
<td>Pt,Pd,Ni/Mg0.95Zr4+0.05O</td>
<td>23.8</td>
<td>3.0</td>
<td>1</td>
<td>0.02 0.029 0.044</td>
</tr>
<tr>
<td>Pt,Pd,Ni/Mg0.85Zr4+0.15O</td>
<td>21.8</td>
<td>6.5</td>
<td>1</td>
<td>0.02 0.029 0.044</td>
</tr>
</tbody>
</table>

Table 1. Preparation of catalyst
prove the mechanical properties and to ensure the MgO and ZrO2 interacts smoothly.

Table 1 lists the steps involved in preparing the Pt,Pd,Ni(acac) 2/Mg1-xZrxO catalysts (1 % concentrations of each Pt, Pd, and Ni metals). First, Pt(C5H7O2)2.H2O (Acros Chemicals; >99%) was used to impregnate 1 % Pt dissolved in dichloromethane for 5 h to produce Pt(acac)2/Mg1-xZrxO. Then, the catalyst was impregnated with 1 % of Pd and Ni each. Pd(C5H7O2)2 (Aldrich; >99.5 %) and Ni(C5H7O2)2.H2O (Acros Chemicals; >99 %) solutions in dichloromethane was used for 5 h for the preparation of the catalysts. The catalysts were dried at 120 °C for 12 h after impregnation in the air. Finally, the catalysts are grind and sieved into particles of sizes 80-150 or 150-250 μm in diameter.

2.2 Characterization catalyst

A diffractometer (Shimadzu model XRD 6000) was used. The radiation process took place in a Philips glass diffraction X-ray tube of broad focus 2.7 kW. The calculation of the size of the crystals is based on the Debye-Scherrer relationship [13].

The Kratos Axis Ultra DLD system is fixed with a monochromatic Al Kα (1486.6 eV) and two X-ray sources (Al & Mg). The operation of the X-ray gun, which is the source of excitation, is based on an emission current of 20 mA combined with 15 kV voltages. The mode of operation for this hemispherical analyzer is based on fixed analyzer transmission (FAT) for wide and narrow scanning. The amount of the pass energy was fixed at 100 eV and 40 eV. The region of interest for the narrow scan and photoelectron signals Mg2p, Zr3d, Pd3d, Ni2d, Pt4f, and O1s correspond to each other. The carbon charging correction refers to the binding energy of 285 eV for adventitious carbon.

The evaluation of the catalysts active site was performed using the temperature programmed reduction (H2-TPR) method that required hydrogen. The apparatus used to perform the evaluation was the Thermo Finnegan TPDRO 1100, attached with a thermal conductivity detector.

The total surface area of the catalyst was calculated using the Brunauer–Emmett–Teller (BET) method with nitrogen adsorption set at -196 °C. Meanwhile, the Thermo Fisher Scientific S.P.A model: Surfer Analyzer) nitrogen adsorption-desorption analyzer was used for analysis.

The apparatus, transmission electron microscopy (TEM) (Hitachi H7100 TEM with an increasing voltage of 10 MV) was used to identify the crystal system and the catalysts homogeneity. The apparatus Mettler Toledo TGD TA (Pt crucibles, Pt/Pt-Rh thermocouple) and a heating range of 50 to 1000 °C, was used to conduct thermogravimetric analysis (TGA).

2.3 Catalytic evaluations

Production of syngas (H2/CO) as the model for the reforming of biogas was conducted using a fixed bed stainless steel micro-reactor (i.d. φ = 6 mm, h = 34 cm) during the catalytic evaluation for DRM. A mass flow gas controller (SIERRA instrument) and an online gas chromatography (GC) (Agilent 6890N; G 1540N) equipped with Varian capillary columns HP-PLOT/Q and HP-MOLSIV were connected to a reactor.

Before the start of the process, the reduction of approximately 0.02 g of the catalyst was conducted by flowing 5 % H2/Ar at 700 °C, and the holding period was 3 h. The aim of the reduction step was to convert the (Ni2+,Pd2+, and Pt2+) phase of the catalyst to the metal (Ni °, Pd°, and Pt °) phase at the active sites of the catalysts. The tested catalyst was held in a vertical position using plugs of quartz wool in the middle of a reactor. A thermocouple was placed into the catalyst chamber to control and check the reaction temperature. The calculations of the conversions for CH4 and CO2, selectivity for H2 and CO, as well as ratios for syngas (H2/CO), were based on Equations (2-6).

3. Results and Discussion

3.1 Characterization of the catalysts

3.1.1 XRD patterns

Figures 1 (a-d) display the XRD patterns of the catalysts with MgO and ZrO2 contents. The
diffraction peaks were observed at \( \theta = 37.0^\circ \) (111), 42.9\(^\circ\) (200), 62.3\(^\circ\) (220), 74.7\(^\circ\) (311), and 79.1\(^\circ\) (222). This occurrence was related to the cubic form of magnesia (JCPDS file no.: 00-002-1207). Meanwhile, the peaks recorded at \( \theta = 17.5^\circ \) (100), 24.1\(^\circ\) (211), 28.3\(^\circ\) (111), 31.5\(^\circ\) (111), 34.2\(^\circ\) (020), 35.4\(^\circ\) (102), 38.6\(^\circ\) (120), 40.8\(^\circ\) (102), 44.8\(^\circ\) (211), 49.3\(^\circ\) (220), 54.1\(^\circ\) (122), 57.9\(^\circ\) (222), 59.8\(^\circ\) (120), 62.3\(^\circ\) (311), 69.0\(^\circ\) (123), and 74.7\(^\circ\) (140) were attributed to the cubic form of zirconia (JCPDS file no.: 00-001-0750). The peaks that were recorded at \( \theta = 24.4^\circ \) (113), 30.3\(^\circ\) (006), 36.0\(^\circ\) (033), 41.4\(^\circ\) (027), 45.6\(^\circ\) (127), 50.7\(^\circ\) (218), 56.3\(^\circ\) (234), 56.0\(^\circ\) (502), 57.2\(^\circ\) (330), 62.5\(^\circ\) (424), 65.7\(^\circ\) (154), 71.3\(^\circ\) (131), and 72.7\(^\circ\) (032) were mainly attributed to the cubic form of the catalyst complex (Mg–Zr–O). As for the catalyst with 1 % Pt, Pd, and Ni for all the patterns, no diffraction peaks were observed. This observation is attributed to the catalyst containing an insubstantial amount of the metals. This observation was similar to the findings by Grange [14].

The Debye-Scherrer equation (Table 2) was used to calculate the diffraction of the highest peak in the XRD patterns. Later, this diffraction value was used to obtain the average crystalline size. The results showed that the size of the crystal and the increasing amount of zirconia in the catalysts was inversely proportional. This occurrence is attributed to the growth of magnesia crystallites due to the effects of the remains of Pt, Pd, and Ni on the sample surface. The size of the crystal was observed at 42.2, 47.7, 45.8, and 43.9 nm for the following catalysts, respectively:

- \( \text{Pt,Pd,Ni/MgO (type 1)} \)
- \( \text{Pt,Pd,Ni/Mg_{0.97}Zr_{0.03}O (type 2)} \)
- \( \text{Pt,Pd,Ni/Mg_{0.93}Zr_{0.07}O (type 3)} \)
- \( \text{Pt,Pd,Ni/Mg_{0.85}Zr_{0.15}O (type 4)} \)

Hence, the cubic crystal system is the most predominant among all the samples. This finding is supported by cubic shaped particles that were observed by TEM and FESEM.

XRF was used for the analysis of elements for all the components in the catalyst. Table 2 lists the percentages of Ni, Pd, and Pt, which are slightly more than 1. This result was mainly attributed to the incomplete precipitation of magnesium and zirconium metal precursors during the process of coprecipitation [15,16].

### 3.1.2 XPS analysis

Figures 2(a-g) illustrates the use of X-ray photoelectron spectroscopy (XPS) for the investigation of wide scan, O1s, Mg2p, Zr3d, Ni2p, Pd3d, and Pt4f of the reduced catalyst Pt,Pd,Ni/Mg_{0.85}Zr_{0.15}O. The following reveals the findings of a study, in which the spectra of the XPS on the surface of a few layers of the catalyst measure 3-12 nm. Figure 2a shows the wide scan of the catalyst, whereas, Figure 2b illustrates five significant oxygen species for O1s. These species are found on the topmost layer of the catalyst assigned to Ni–O, Zr–O, Mg–O, Pt–O, and Pd–O at binding energies of 528.1, 529.0, 531.9, 533.2, and 534.3 eV, re-

![Figure 1. XRD patterns of the catalysts: (a) Pt,Pd,Ni/MgO, (b) Pt,Pd,Ni/Mg_{0.97}Zr_{0.03}O, (c) Pt,Pd,Ni/Mg_{0.93}Zr_{0.07}O, (d) Pt,Pd,Ni/Mg_{0.85}Zr_{0.15}O](image-url)

### Table 2. Particle size measurement by XRD, TEM and XRF results

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>TEM (nm)</th>
<th>Crystal size (D)</th>
<th>Debye-Sherrer eq. (nm)</th>
<th>Ni%</th>
<th>Pd%</th>
<th>Pt%</th>
<th>Mg &amp; Zr%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt,Pd,Ni/MgO</td>
<td>49</td>
<td>42.2</td>
<td>1.13</td>
<td>1.09</td>
<td>1.15</td>
<td>95.50</td>
<td></td>
</tr>
<tr>
<td>Pt,Pd,Ni/Mg_{0.97}Zr_{0.03}O</td>
<td>60</td>
<td>47.7</td>
<td>1.18</td>
<td>0.91</td>
<td>1.14</td>
<td>96.33</td>
<td></td>
</tr>
<tr>
<td>Pt,Pd,Ni/Mg_{0.93}Zr_{0.07}O</td>
<td>53</td>
<td>45.8</td>
<td>1.03</td>
<td>1.13</td>
<td>1.18</td>
<td>96.2</td>
<td></td>
</tr>
<tr>
<td>Pt,Pd,Ni/Mg_{0.85}Zr_{0.15}O</td>
<td>47</td>
<td>43.9</td>
<td>0.93</td>
<td>0.89</td>
<td>1.07</td>
<td>95.9</td>
<td></td>
</tr>
</tbody>
</table>

Copyright © 2018, BCREC, ISSN 1978-2993
Figure 2. XPS narrow scans of the reduced catalyst: a) wide scan, b) O1s, c) Mg2p, d) Zr3d, e) Ni2p, f) Pd3d, g) Pt4f
spectively. Figure 2c shows one significant peak, obtained from Mg2p, bulk Mg–O at a binding energy of 49 eV. Meanwhile, Figure 3d provides an illustration of Zr3d of ZrO2 with BE from 924 eV to 875.2 eV. The most intense photoelectron signal is that of Zr–O, which lies in the high BE region. The peaks are observed at 887.3 eV and 882.4 eV. The width of the Ni2p3/2 spectrum is 29 eV, consisting of four main peaks due to the presence of Ni–O (Figure 2e). Four peaks are present in Pt4f and two peaks for Pd3d, which is due to the presence of Pt4f5/2 and Pt4f7/2 that appear in the range of 74–66 eV in the catalyst (Figures 2 e-f) [17,18].

3.1.3 H2-TPR

The TPR analysis were carried out on the following catalysts to examine their reduction behavior:
- Pt,Pd,Ni/MgO (type 1)
- Pt,Pd,Ni/Mg0.97Zr4+0.03O (type 2)
- Pt,Pd,Ni/Mg0.93Zr4+0.07O (type 3)
- Pt,Pd,Ni/Mg0.85Zr4+0.15O (type 4)

Figures 3(a-d) and Table 3 illustrate the TPR profiles of these catalysts. Figure 3a illustrates three well-defined reduction peaks in the TPR profile of the Pt,Pd,Ni/MgO. The first reduction peak is shown at 130 °C. This result is related to the reduction of the PtO species when Pt° is being produced, in comparison with a study conducted by Mahoney et al. [19] who detected the reduction of the PtO species at 114 °C. The second reduction peak, which is recorded at 184 °C, is due to the reduction of PdO to Pd°. The third and last peak is recorded within the region with a temperature of 511 °C due to the strong interaction of the supporting material to produce Ni. This is possible as the NiO species are very few. In a study conducted by Bao et al. [20], a reduction was observed in the NiO for the catalyst of Ni/ZrMgAl at 516 °C.

Figures 3(b-d) and Table 3 provide the TPR profile for catalysts including the ZrO2 promoter. The TPR profiles of the catalysts (Type 2, 3, and 4) are not similar to that of the catalyst of Pt,Pd,Ni/MgO. One of the differences depends on the number of peaks. Results show five peaks. The first three peaks of the Pt,Pd,Ni/Mg0.97Zr4+0.03O catalyst were recorded at 115, 173, and 495 °C. Peaks of the Pt,Pd,Ni/Mg0.93Zr4+0.07O catalyst were shown at 123, 204, and 473 °C, while peaks of the Pt,Pd,Ni/Mg0.85Zr4+0.15O catalyst were observed at 170, 192, and 484 °C. This condition is due to the reduction of PtO, PdO, and NiO that occurred on the top most layer of catalysts in obtaining the Pt°, Pd°, and Ni° elements, respectively. The fourth peak for the catalysts (Type 2, 3, and 4) was recorded when the temperatures were 532, 545, and 559 °C, respectively. The findings corresponded to the reduced amount of ZrO2 on the surface. Thus, when the temperature of the catalysts dropped, a significant lowering was observed on the ZrO2 surface. A few reasons for this occurrence were as follows: The first reason could be linked to the well-dispersed ZrO2 particles during the process of incorporation of MgO into ZrO2 and the retardation of sintering [21]. The other reason could be due to the occurrence when ZrO2 and Pt, Pd, and Ni metals interact actively during the overlapping of PtO, PdO, NiO, and ZrO2 in reducing the peaks. The fifth peak was formed at 635, 652, and 677 °C, respectively. Strong interactions exist between the species of the

| Table 3. H2-TPR values of the different catalysts |
|------------------------------------------|----------|----------|----------|----------|----------|------------------|
|                                          |          |          |          |          |          | sorbed H2 gas  |
|                                          |          |          |          |          |          | (µmol/g)        |
| Pt,Pd,Ni/MgO                             | 130      | 184      | 511      | -        | -        | 488.6           |
| Pt,Pd,Ni/Mg0.97Zr4+0.03O                 | 115      | 173      | 495      | 532      | 635      | 503.7           |
| Pt,Pd,Ni/Mg0.93Zr4+0.07O                 | 123      | 204      | 473      | 545      | 652      | 517.9           |
| Pt,Pd,Ni/Mg0.85Zr4+0.15O                 | 170      | 192      | 484      | 559      | 677      | 523.4           |

Copyright © 2018, BCREC, ISSN 1978-2993
ZrO₂ promoter and the MgO support with the reduction of bulk ZrO₂. Catalysts showed a higher degree of reducibility when the loading of the promoter increased. This finding was similar to results obtained from previous studies. Rotaru et al. [21] reported that the reduction of zirconium occurred at 490 and 790 °C. Their findings also revealed that the promoters were well-dispersed for the support, and the interaction between the support with doping Pt, Pd, and Ni species was high. The other finding stated that the significant peak of TPR profile was formed at temperatures ranging from 684 °C to 737 °C. Thus, ZrO₂ alone was capable of reducing the range in temperatures [22]. Another obvious finding pointed out that the addition of the ZrO₂ promoter was effective in the reducibility of catalysts with MgO support. Mg₁₋ₓZr₄₊ₓO, which recorded a higher basicity than MgO, showed more interaction with the ZrO₂ promoter. Consequently, PtO, PdO, and NiO were reduced more significantly because of the redox property of Mg₁₋ₓZr₄₊ₓO [23].

The total amount of H₂ consumed during the reduction of the catalysts (type 1, 2, 3, and 4) was calculated from the total peak area. The calculations for these catalysts were recorded at 488.6, 503.7, 517.9, and 523.4 µmol/g catalyst, respectively. According to H₂-TPR results, the most active catalyst was Pt,Pd,Ni/Mg₀.₈₅Zr₄₊₀.₁₅O, which suggests that it was the most suitable catalyst for DRM reaction.

3.1.4 BET surface area

Table 4 tabulates the surface area, pore radius, and pore volume of the support MgO and for the Pt,Pd,Ni/Mg₁₋ₓZrₓO catalysts (where x = 0.00, 0.03, 0.07, and 0.15). The surface area for Pt,Pd,Ni/MgO catalyst with a cubic structure supported with TEM was recorded at 12.4 m²/g, while the surface area for the support MgO was recorded at 11.1 m²/g. The former recorded a higher value because of the consequences of the Pt, Pd, and Ni loadings on the specific surface area of the MgO support. In such cases, the surface areas of Pt,Pd,Ni/MgO catalyst was substantially smaller than that of the conventional catalyst (type 2, 3, and 4) which were at 16.7, 17.1, and 18.9 m²/g, respectively. The main reason was the presence of layers of Pt, Pd, and Ni particles partially covering the magnesia pores. The BET surface area of MgO that was promoted by ZrO₂ was nearly similar to one of the common Pt, Pd, and Ni catalysts with binary support [24]. Meanwhile, the features of the supported Pt, Pd, and Ni catalysts with a cubic structure revealed very low metal dispersion and small surface areas of Pt and Pd with few Ni particles. This occurrence is due to the highly interactive activity between the layers of Pt, Pd, and Ni and the support of MgO with the ZrO₂ promoter. The pore volume of Pt,Pd,Ni/Mg₀.₈₅Zr₄₊₀.₁₅O catalyst was 0.19 cm³/g. This value was slightly higher than that of Pt,Pd,Ni/Mg₀.₉₇Zr₄₊₀.₀₃O and Pt,Pd,Ni/Mg₀.₉₃Zr₄₊₀.₀₇O catalysts, which were 0.11 and 0.18 cm³/g, respectively. This finding was different from the study of Bao et al. [20], where the pore volume of NiCeMgAl catalyst was 0.51 cm³/g.

Table 4 illustrates the pore radius of various catalysts. The pore size of the support MgO was 9.9 Å; whereas, the pore size of Pt,Pd,Ni/MgO catalyst was 9.7 Å. The pore radius of the other catalysts and the increase of the ZrO₂ promoter in the support were inversely proportionate to one another. The pore radii of the catalysts (type 2, 3, and 4) were 23.9 Å, 23.5 Å, and 23.2 Å, respectively [25]. These data showed that Pt,Pd,Ni/Mg₀.₈₅Zr₀.₁₅O catalyst with a high surface area recorded better performance in the DRM reaction compared with other catalysts.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Specific surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>11.1</td>
<td>0.21</td>
<td>9.9</td>
</tr>
<tr>
<td>Pt,Pd,Ni/MgO (type 1)</td>
<td>12.4</td>
<td>0.21</td>
<td>9.7</td>
</tr>
<tr>
<td>Pt,Pd,Ni/Mg₀.₈₅Zr₄₊₀.₀₂O (type 2)</td>
<td>16.7</td>
<td>0.11</td>
<td>23.9</td>
</tr>
<tr>
<td>Pt,Pd,Ni/Mg₀.₈₅Zr₄₊₀.₀₇O (type 3)</td>
<td>17.1</td>
<td>0.18</td>
<td>23.5</td>
</tr>
<tr>
<td>Pt,Pd,Ni/Mg₀.₈₅Zr₄₊₀.₁₂O (type 4)</td>
<td>18.9</td>
<td>0.19</td>
<td>23.2</td>
</tr>
<tr>
<td>Spent catalyst</td>
<td>19.3</td>
<td>0.14</td>
<td>24.7</td>
</tr>
</tbody>
</table>
3.1.5 TEM characterization

Figures 4(a-d) show TEM images of Pt,Pd,Ni/MgO (type 1), Pt,Pd,Ni/Mg$_{0.97}$Zr$_{0.03}$O (type 2), Pt,Pd,Ni/Mg$_{0.93}$Zr$_{0.07}$O (type 3), and Pt,Pd,Ni/Mg$_{0.85}$Zr$_{0.15}$O (type 4) catalysts with cubic structures. The catalysts underwent calcination at 1150 °C with uniformity in the distribution of particles but without free ZrO$_2$. Figures 4(b-d) confirms the formation of MgO-ZrO$_2$ solid solutions [26] with cubic oxide particles on the Pt, Pd, and Ni layers of the supported metal. The Pt,Pd,Ni/Mg$_{0.85}$Zr$_{0.15}$O catalyst (Figure 4d) dispersed 1% of the Pt, Pd, and Ni metal particles each for the support magnesia-zirconia of sizes between 45 to 85 nm [27]. In addition, TEM analysis of the Pt,Pd,Ni/Mg$_{0.85}$Zr$_{0.15}$O catalyst indicated an induced growth with an agglomeration of the nanoparticles at a specific distance between the metal crystallites. Often, this type of growth was catalyzed by metallic platinum, palladium, and nickel, although the distribution of TEM image sizes showed more realism.

Figure 4. TEM image of catalysts: (a) Unreduced Pt,Pd,Ni/MgO, (b) Unreduced Pt,Pd,Ni/Mg$_{0.97}$Zr$_{0.03}$O, (c) Unreduced Pt,Pd,Ni/Mg$_{0.93}$Zr$_{0.07}$O, (d) Unreduced Pt,Pd,Ni/Mg$_{0.85}$Zr$_{0.15}$O, (e) Reduced Pt,Pd,Ni/Mg$_{0.85}$Zr$_{0.07}$O with 5% H$_2$ in Ar at 700 °C, (f) Pt,Pd,Ni/Mg$_{0.85}$Zr$_{0.15}$O after 200 h reaction, at 900 °C, and CH$_4$/CO$_2$ ratio 1:1.
and accuracy [28]. Figures 4(a-e) show the TEM results, which are in agreement with XRD data. These results showed that Mg–Zr–O was not only complex but also cubical, similar to MgO and ZrO₂.

3.1.6 Thermal analysis

Figures 5(a-d) show TGA for the Pt,Pd,Ni/MgO (type 1), Pt,Pd,Ni/Mg₀.₉₇Zr⁴+₀.₀₃O (type 2), Pt,Pd,Ni/Mg₀.₉₃Zr⁴+₀.₀₇O (type 3), and Pt,Pd,Ni/Mg₀.₈₅Zr⁴+₀.₁₅O (type 4) catalysts. Results indicated a weight loss, however, it occurred at only one phase of the thermal process. The amount of weight loss was approximately 4 % at temperatures ranging from 100 to 120 °C. This effect was due to the removal of moisture from the Pt,Pd,Ni/Mg₁₋ₓZrxO catalyst. On one hand, the catalysts (type 1, 2, 3, and 4) involve weight loss at 2.5, 2.3, 2.6, and 2.7%, respectively. On the other hand, Pt,Pd,Ni/Mg₀.₈₅Zr⁴+₀.₁₅O (type 4) and Pt,Pd,Ni/Mg₀.₈₂Zr⁴+₀.₀₇O (type 3) catalysts (See Figures 5(c-d)) showed further weight loss at 2.3 % and 2.7 %, respectively, at the second stage. This effect was due to the oxygen atoms removed from the catalyst. From the graph, the initial findings revealed that the entire weight of the compound showed a slight increase, because the compound adsorbs the N₂ gas in the machine. All the compounds remained stable at 600 °C. This result was attributed to the high melting point of magnesia and zirconia at 2852 and 2177 °C, respectively. From Figures 5(a-d), the components of the catalyst interacted well with one another. These findings are similar with the results obtained by Mojovic et al. [29].

3.2 Catalytic performance in biogas reforming

3.2.1 Effects of reactant concentration on conversion

The conversion of CH₄ and CO₂ indicates the reactive activity of the DRM, while the H₂/CO ratio expresses the selectivity. The blank test results, where no catalyst was used, indicated the H₂ and CO presence in the outlet gas when the temperature was set above 900 °C. This occurrence resulted from the decomposition of methane (Equation 7). When Mg₁₋ₓZrxO was used in the absence of other metals, the conversion of CH₄ and CO₂ was very low, with recording of 36 % and 50 %, respectively; whereas, the H₂/CO ratio was recorded at 0.3 %. These findings indicate a weak reaction occurred in the pores of the support promoter. Meanwhile, BET results also revealed similarity; the presence of pores in the catalyst. On the contrary, an increase in the conversion of CH₄ and CO₂ and the H₂/CO ratio was observed (Figure 6) when Pt,Pd,Ni/Mg₁₋ₓZrxO catalysts were used. Hence, Pt, Pd, and Ni metals doped on the support have a significant effect in the catalytic reaction. Pt,Pd,Ni/Mg₀.₈₅Zr⁴+₀.₁₅O (type 4) catalyst recorded CH₄ and CO₂ conversion of 91 % and 99 %, respectively, in the 1:1 ratio for CH₄:CO₂ and 1.28 for H₂:CO ratio. The conversion of the gases recorded CH₄ and CO₂ conversion of 85 % and 96 %, respectively, in the reactant ratio (2:1) and 1.16 for H₂:CO ratio. These findings revealed that the 1:1 ratio is the most effective in resisting the deactivation of the catalyst for carbon deposition and high selectivity of H₂
and CO (Figure 6). Meanwhile, the remaining catalysts are similar in this characteristic [30].

\[
\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \quad \Delta H_{298}^\circ = 75.0 \text{ kJ/mol} \quad (7)
\]

### 3.2.2 Effects of concentration of catalyst on conversion

Figure 7 and Table 5 illustrate the consequences of varying concentration levels of the catalyst during the conversion process. The conversion of \( \text{CH}_4 \), \( \text{CO}_2 \), and the \( \text{H}_2/\text{CO} \) ratio showed that the catalysts were arranged in an order, where \( \text{Pt},\text{Pd},\text{Ni}/\text{MgO} < \text{Pt},\text{Pd},\text{Ni}/\text{Mg}_{0.97}\text{Zr}_{0.03} < \text{Pt},\text{Pd},\text{Ni}/\text{Mg}_{0.93}\text{Zr}_{0.07} < \text{Pt},\text{Pd},\text{Ni}/\text{Mg}_{0.85}\text{Zr}_{0.15} \). The main catalysts, namely, Pt and Pd with Ni and the support, MgO-ZrO\(_3\) were combined together. Experiments were conducted at 900 °C and 1 atm with a 1:1 reactant ratio (\( \text{CH}_4:\text{CO}_2 \)) (Figure 7 and Table 5). In the conversion of methane, the highest reading was recorded for the \( \text{Pt},\text{Pd},\text{Ni}/\text{Mg}_{0.85}\text{Zr}_{0.15} \) (91 %) catalyst; whereas, the lowest reading was found in the \( \text{Pt},\text{Pd},\text{Ni}/\text{MgO} \) (75 %) catalyst. The other finding revealed that many catalysts that were tested showed a slight deactivation after 200 h.

**Figure 7.** The effect of using different catalysts 1) \( \text{Pt},\text{Pd},\text{Ni}/\text{MgO} \), 2) \( \text{Pt},\text{Pd},\text{Ni}/\text{Mg}_{0.97}\text{Zr}_{0.03} \), 3) \( \text{Pt},\text{Pd},\text{Ni}/\text{Mg}_{0.93}\text{Zr}_{0.07} \), and 4) \( \text{Pt},\text{Pd},\text{Ni}/\text{Mg}_{0.85}\text{Zr}_{0.15} \) on \( \text{CH}_4,\text{CO}_2 \) conversion and \( \text{H}_2/\text{CO} \) ratio at 900 °C for the 1:1 ratio of \( \text{CH}_4:\text{CO}_2 \)

In general, the \( \text{CO}_2 \) conversion recorded more stability than the \( \text{CH}_4 \) conversion. As for the conversion of \( \text{CO}_2 \), the \( \text{Pt},\text{Pd},\text{Ni}/\text{Mg}_{0.85}\text{Zr}_{0.15} \) (99 %) catalyst provided the highest rate of conversion; whereas, the \( \text{Pt},\text{Pd},\text{Ni}/\text{MgO} \) (86 %) catalyst revealed the lowest rate of conversion. These results showed that the catalyst of \( \text{Pt},\text{Pd},\text{Ni}/\text{Mg}_{0.85}\text{Zr}_{0.15} \) is the most effective catalyst in the conversion process.

The value of the product ratio of \( \text{H}_2/\text{CO} \) for catalysts (Figure 7 and Table 5) was more than 1. These findings indicated that the process of \( \text{CO}_2 \) conversion of Ni metal showed less favorable results than that of the tri-metallic catalysts compared with a previous study [20]. However, an evidence of improvements was observed in the side reactions indicated by the differences between the conversions and the product yields. Table 5 presents evidence that an increase in the concentration level of zirconia was followed by an increase in the conversion rate of \( \text{CH}_4 \) and \( \text{CO}_2 \) as well as the \( \text{H}_2/\text{CO} \) ratio. The \( \text{Pt},\text{Pd},\text{Ni}/\text{Mg}_{0.85}\text{Zr}_{0.15} \) catalyst produces an excellent result at the site with most activity of \( \text{H}_2\)-TPR and it also produced the outstanding BET result from the large surface area.

**Table 5.** The catalytic results of DRM reaction for the catalysts at 900 °C for the 1:1 ratio of \( \text{CH}_4:\text{CO}_2 \)

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>( \text{CH}_4 ) Conversion %</th>
<th>( \text{CO}_2 ) Conversion %</th>
<th>( \text{H}_2/\text{CO} ) ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pt},\text{Pd},\text{Ni}/\text{MgO} )</td>
<td>75</td>
<td>86</td>
<td>1.07</td>
</tr>
<tr>
<td>( \text{Pt},\text{Pd},\text{Ni}/\text{Mg}<em>{0.97}\text{Zr}</em>{0.03} )</td>
<td>86</td>
<td>94</td>
<td>1.12</td>
</tr>
<tr>
<td>( \text{Pt},\text{Pd},\text{Ni}/\text{Mg}<em>{0.93}\text{Zr}</em>{0.07} )</td>
<td>88</td>
<td>97</td>
<td>1.15</td>
</tr>
<tr>
<td>( \text{Pt},\text{Pd},\text{Ni}/\text{Mg}<em>{0.85}\text{Zr}</em>{0.15} )</td>
<td>91</td>
<td>99</td>
<td>1.28</td>
</tr>
</tbody>
</table>

This occurrence reveals that the addition of \( \text{ZrO}_2 \) into the \( \text{MgO} \) catalysts can significantly reduce the reverse water-gas shift (RWGS) reaction (Equation 8).

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H_{298}^\circ = \text{41.0 kJ/mol} \quad (8)
\]

Results also indicated that the CO formation rate in the DRM reaction depended on the strong interaction between the \( \text{ZrO}_2 \) promoter and the support \( \text{MgO} \) in solid solution. The findings are as follows: the ratio of mole in the catalyst is 0.15:0.85, the biggest surface area is 18.9 m\(^2\)/g (Table 4), and the site with the most activity has 523.4 μmol/g from the total amount of \( \text{H}_2 \)-consumption provided evidence for \( \text{H}_2\)-TPR study (Table 3). Thus, the process of forming a solid solution was important in the production of active sites for the \( \text{CO}_2 \) reforming of methane.
The presence of the entire ZrO₂ promoter as a solid solution stabilized the two oxides. When hydrogen was reduced at 700 °C, only the surface layer of the ZrO₂ solid solution of the ZrO₂-MgO catalyst was shrunk. Moreover, the Zr sites produced remained close to the solid solution, thereby causing an obstacle to Zr sintering [31]. Moreover, the sites that affected the catalytic process were found in the Pt, Pd, and Ni particles causing abundant interaction between the Pt, Pd, and Ni particles and MgO-ZrO₂. When the Pt, Pd, and Ni concentration levels in the support increased, the CH₄ and CO₂ conversion and selectivity did not show any significant change. This occurrence could be due to the formation of nanoparticles, which is the consequence of the XRD (Debye Sherrer’s equation) and TEM results (Table 2).

Despite the use of X-ray diffraction for a simplistic and possible estimation of the crystal size from the widening of the XRD reflections through the use of Scherrer’s formula, the nanoparticulation of the particles was preferred. The nanoparticles selected as catalysts for this study maximized the surface area and secured more reactions. Moreover, these catalysts allowed the Pt, Pd, and Ni metals to be dispersed effectively on the surface of the catalysts. These catalysts also provided strong Lewis basicity with metal oxide support. Furthermore, the increase in the support for Lewis basicity enhanced the ability of the catalyst to chemisorb CO₂ in the DRM reaction. Subsequently, the formation of CO occurred when the adsorbed CO₂ reacted with deposited carbon (Equation 9) with less formation of coke.

$$\text{CO}_2 + \text{C} \rightarrow 2\text{CO} \quad \Delta H_{298^\circ} = +172 \text{ kJ/mol} \quad (9)$$

XPS results suggested the use of a special approach, which is the formation of the ZrO₂-MgO solid solution, to prevent carbon deposition. MgO is a strong Lewis base and has a high adsorption of CO₂ in the reduction or prevention of carbon deposition. Besides, the reduction of ZrO₂ in the ZrO₂-MgO solid solution was more difficult, often causing the smaller particles of zirconium to be formed on the topmost layer compared with that of unadulterated ZrO₂ [32,33]. When surface basicity combines with the particle size of small metals, the MgO-based solid solution catalyst can prevent carbon deposition more effectively. Despite a more realistic and accurate distribution of TEM images in terms of size, several drawbacks existed in the images.

The high readings in the conversion of CH₄ and CO₂ were due to the involvement of the particle size in the reactive activity which recorded the best result. Moreover, the preparation of Pt, Pd, and Ni doping metals was based on the Debye-Sherrer equation and the support of TEM analysis. The metal size was as nanoparticles. Therefore, the particle size is crucial in the activity of the reaction. Another finding reported that when the size of the particles had been reduced to nano range, an increase in the conversion of the reactants and selectivity was observed. This result was supported by findings of more activities which were recorded at 523.4 µmol/g in the active sites and at 18.9 m²/g in the surface area (Tables 3 and 4).

### 3.2.3 Effects of temperature on conversion

Figure 8 presents the results of the selectivity and activity of Pd,Pd,Ni/Mg₀.₈₅Zr₄⁺₀.₁₅O catalyst from 700 to 900 °C. The conversion of CH₄:CO₂ (1:1) increased when the temperature was raised from 700 to 900 °C. During the DRM, the strong endothermic reaction (Equation 1) and a higher increase in temperature in the conversion rate have contributed to the increase in the conversion ratio of CH₄:CO₂. This occurrence has been reported in earlier research [34]. The CH₄ conversion of Pd,Pd,Ni/Mg₀.₈₅Zr₄⁺₀.₁₅O increased from 45 to 91 % when the temperature was raised from 700 to 900 °C. Meanwhile, the CO₂ conversion increased from 56 to 99 %. For temperatures of more than 900 °C, no significant increase occurred in the CH₄ and CO₂ conversions. Figure 8 shows the H₂/CO ratio of the catalyst for different temperatures. When the temperature was <900 °C, the H₂/CO ratio of the samples was <1. This occurrence was due to the RWGS (Equation 8) that consumed more H₂ and simultaneously produced CO, resulting in the lowering of H₂/CO ratio. The H₂/CO ratio of Pd,Pd,Ni/Mg₀.₈₅Zr⁺₁.₁₅O was 1.28 when the temperature was 900 °C. This result indicates that the RWGS reaction (Equation 8) causes slight effect [7] because the concentration of hydrogen will remain high while the concentration of carbon monoxide is low and therefore the H₂/CO ratio remains high.

### 3.2.4 Stability tests

Figure 9 presents the result obtained from the test involving temperature. Results showed that the CH₄ and CO₂ conversion rate was high at 900 °C. In this mechanism, the reaction between a molecule of methane and Ni surface (Nickel has the best conversion among other metals due to its size and high density of posi-
ative charge \cite{10} ) produced desorbed hydrogen and hydrocarbon species \( \text{CH}_x \) \( (x = 0-4) \); when \( x=0 \), carbon deposits on the Ni metal surface \cite{35}. Equations 10-14 are shown below:

\[
\begin{align*}
\text{CH}_4 + 2\text{Ni(as)} & \rightarrow \text{CH}_3\text{Ni(as)} + \text{HNi(as)} \quad (10) \\
\text{CH}_3\text{Ni(as)} + \text{Ni(as)} & \rightarrow \text{CH}_2\text{Ni(as)} + \text{HNi(as)} \quad (11) \\
\text{CH}_2\text{Ni(as)} + \text{Ni(as)} & \rightarrow \text{CHNi(as)} + \text{HNi(as)} \quad (12) \\
\text{CHNi(as)} + \text{Ni(as)} & \rightarrow \text{CNi(as)} + \text{HNi(as)} \quad (13) \\
2\text{HNi(as)} & \rightarrow \text{H}_2 + 2\text{Ni(as)} \quad (14)
\end{align*}
\]

(a) metal active site

Nakamura et al. \cite{36} described the effects of a promoter on the catalyst during the DRM through an increase in the dispersion of Pt, Pd, and Ni. One of the effects was the activation of carbon dioxide on the support-promoter that had been mixed with the metal particle for the formation of a carbonate species. Subsequently, the \( \text{CH}_x \) species reduced the carbonate substrate to form carbon monoxide (CO) (Equations 15-19).

\[
\begin{align*}
\text{CO}_2(g) & \rightarrow \text{CO}_2\text{(support)} \quad (15) \\
\text{CO}_2\text{(support)} + \text{O}^{-2}\text{(support)} & \rightarrow \text{CO}_3^{-2}\text{(support)} \quad (16) \\
2\text{H(metal)} & \rightarrow 2\text{H(support)} \quad (17) \\
\text{CO}_3^{-2}\text{(support)} + 2\text{H(support)} & \rightarrow \text{HCO}_2^{-1}\text{(support)} + \text{OH}^{-1}\text{(support)} \quad (18) \\
\text{CO}\text{(support)} & \rightarrow \text{CO}\text{(g)} \quad (19)
\end{align*}
\]

As it is well known that carbon deposited on the metal surface will decrease the stability of the catalysis but the presence of ZrO\(_2\) promoter will remove the deposited carbon and reactivated the catalyst. The presence of the ZrO\(_2\) promoter in the catalyst was mainly to secure a very stable platform and strong resistance to coking that may occur when CO\(_2\) and CH\(_4\) are being converted as well as the H\(_2\)/CO ratio for reactions of 200 h or more. The carbon formed on the catalyst was removed by ZrO\(_2\) during the DRM reaction. Moreover, the enhancement of CO\(_2\) adsorption occurred in the presence of ZrO\(_2\) because it can increase the basicity. This phenomenon was closely followed by the formation of carbonate species, particularly ZrO\(_2\) that is capable of breaking down CO\(_2\) into CO and O. Finally, the O atom is moved to Zr promoter. At the last stage, the O atom combined with the C that deposits on the metal catalyst had produced CO \cite{37}. Based on the findings, a significant decline in the carbon deposition on the catalyst was observed (Equations 20-21).

\[
\begin{align*}
\text{CO}_2(g) & \rightarrow \text{CO}\text{(support)} + \text{O}\text{(promoter)} \quad (20) \\
\text{C(metal)} + \text{O}\text{(promoter)} & \rightarrow \text{CO}_2(g) \quad (21)
\end{align*}
\]

In the case of a low ZrO\(_2\) concentration, the CO\(_2\) conversion indicated active formation of strong ionic oxides, such as ZrOOCO\(_3\), which attracted CO\(_2\) to the topmost layer of the catalyst that subsequently increases the CH\(_4\) conversion rate. In the case of a high ZrO\(_2\) concentration, the conversion rate for both CH\(_4\) and CO\(_2\) declined. The decrease could be attributed to the higher electron density of Pt, Pd, and Ni \cite{38}. The decomposition of the ZrOOCO\(_3\) species in DRM has produced CO and an oxygen species that react with the carbon deposits on the interface of Pt, Pd, and Ni-ZrO\(_2\) thus reviving the activity sites of the Pt, Pd, and Ni. ZrO\(_2\) supported catalysts similarly facilitated the dissociation of adsorbed CO\(_2\). Besides its promotional effect on CO\(_2\), the dissociative adsorption of zirconia has improved the dispersion

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{The influence of temperature on the catalytic activity of the Pt,Pd,Ni/Mg\(_{0.85}\)Zr\(_{0.15}\)O catalysts: 1) 700 °C, 2) 800 °C, 3) 900 °C for the 1:1 ratio of CH\(_4\):CO\(_2\) at 900 °C in 1:1 ratio.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{Stability tests of Pt,Pd,Ni/Mg\(_{0.85}\)Zr\(_{0.15}\)O catalysts at 900 °C for the 1:1 ratio of CH\(_4\):CO\(_2\), for 200 h. (GHSV = 15000 ml.gcat\(^{-1}\).h\(^{-1}\), atmospheric pressure)}
\end{figure}
and stabilization of small metal particles. In fact, zirconia is an oxide with proven ability to have strong interaction during the support metallic phase; hence, significant changes occurred in the surface properties of both the oxide and metal [39].

The activity and stability of the Ni, Pd, and Pt tri-metallic catalyst had better results than that of the mono-metallic Ni or Pd-Ni catalyst and Pt-Ni bi-metallic catalysts (Table 3 and Figure 8). This may have attributed to the fact that the Pd and Pt transfer the electron density to their Ni metal (main catalyst) in the tri-metallic catalyst, as described in our previous work (10). This result is consistent with the hypothesis that Pt and Pd can prevent the oxidation of Ni as its electron density increases [40,41]. When the Pt-Ni or Pd-Ni bi-metallic cluster is formed, the reducibility of Ni increased. In such cases, the activities for more than 200 h are higher and more stable [12,42].

3.2.5 Post-reaction characterization

TGA and TEM images indicated the presence of very low concentration of coke deposit of the spent catalyst. Figure 4f shows TEM images of the spent catalysts that reveal similar structure of the catalyst was intact even after it had undergone stream testing for 200 h. Moreover, no change occurred in the two-dimensional cubic texture of the spent catalyst. TEM results showed layered deposition of the carbon with no traces of filamentous carbon. However, the pore size of the spent catalyst showed a remarkable increase from 23.2 Å to 24.7 Å. BET analysis also revealed that the surface area of the spent catalyst had increased slightly from 18.9 to 19.3 m²/g. A slight metal sintering was also observed in the spent catalyst. Although the cubic channel of the used catalyst indicated that the sintering of the active metals inside the pore was limited, the active metals that supported the outer surface experienced significant sintering. A negligible coke deposition occurred because of the absence of filamentous carbon in the used catalyst.

Figure 10 presents TGA with an oxygen stream of post-reaction of the catalyst Pt,Pd,Ni/Mg0.85Zr4+0.15O, and the calculation of weight change for each temperature range with reference to the thermogram, three different regions with different ranges in temperature exist. The temperature range in the first region is low because of the weight increase in the spent catalyst. The temperature range in the second region is of mid-range, whereby the weight of the spent catalyst declined. The temperature range in the third region is of high range because of the weight increase in the spent catalyst. The weight increase is due to the oxidation of Ni particles at temperatures higher than 100 °C. Zhu et al. [43] reported that the weight increase in the spent catalyst was lower than 3%. The compound showed increased slightly when the temperature range was at 150-500 °C; whereas, the weight loss at 650 °C was due to the oxidation of deposited carbon.

The calculation of the coke deposition on the spent catalyst amounted to 1.6 wt %. Finally, all the elements on the topmost layer were oxidized by oxygen after removing the carbon found on the topmost layer as CO₂. Thus, it can be obtained at 900 °C. A very small amount of coke is deposited on the topmost layer of the
catalyst because of the good metals dispersed in the catalysts, and the smaller crystal metal catalysts do not deactivate easily because of their nanoparticle size.

3.2.6 Enhancing the catalyst

DRM reaction can be improved with experiments conducted in low oxygen concentration flow (1.25 %). Figure 11 presents data that show improvement in the conversion of CH₄ from 91 to 96 %. This improvement is achieved by adding an oxidant (O₂) to partially or completely oxidize methane together with the use of exothermicity in the reaction that supplies the necessary direct heat to the DRM reactant mixture [38]. However, this process does not affect the CO₂ conversion and the H₂/CO ratio because of the reaction between oxygen and CH₄ to produce CO and H₂O (Equation 22). This is followed by the reaction between the steam and the deposited carbon to produce syngas (Equation 23). Coke deposition is also reduced because of the presence of O₂ on the catalyst (Equation 24). Thus, this process has not only decreased the amount of carbon deposition but also improved the lifespan of the catalyst.

\[
\begin{align*}
\text{CH}_4 + 1.5\text{O}_2 & \rightarrow \text{CO} + 2\text{H}_2\text{O} \quad (22) \\
\text{C}_{(s)} + \text{H}_2\text{O} & \rightarrow \text{CO} + \text{H}_2 \quad (23) \\
\text{C}_{(s)} + \text{O}_2 & \rightarrow \text{CO}_2 \quad (24)
\end{align*}
\]

4. Conclusion

Dry reforming of methane over Ni,Pd,Pt/Mg₁₋ₓZrxO catalysts were carried out for the production of syngas. The catalysts were synthesized using co-precipitation method with K₂CO₃ as the precipitant. The catalysts were characterized for its physicochemical properties by XRD, XRF, XPS, H₂-TPR, BET, TEM, and TGA. Ni,Pd,Pt/Mg₀.₈₅Zr₀.₁₅O catalyst exhibited the highest activity resulting in favorable CO₂ and CH₄ conversion rates of 99 % and 91 %, respectively, and a suitable H₂/CO ratio 1.28 at temperature 900 °C and 1:1 of CH₄:CO₂ ratio. The different results of the catalysts showed that the catalytic performances of the catalysts strongly depended on the nature and concentration of promoter. The stability of Ni,Pd,Pt/Mg₀.₈₅Zr₀.₁₅O catalyst was investigated for 200 h, and in the presence of 1.25 % stream of oxygen the stability was increased, resulting in a decrease in the coke deposition and a high conversion of CH₄ which increased from 91 to 96 %.

Acknowledgement

The researcher are grateful to NanoMite Grant (Vot. No: 5526308) for the provision of the necessary funds for conducting this research study. I expresses heartfelt thanks to Prof. Taufiq Yap Yun-Hin for his help and introduce all facilities.

References


