CNT and H₂ Production During CH₄ Decomposition over Ni/CeZrO₂. I. A Mechanistic Study

Agata Łamacz

Division of Chemistry and Technology of Fuels, Wroclaw University of Science and Technology, Gdanska 7/9, 50-344 Wroclaw, Poland; agata.lamacz@pwr.edu.pl

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Abstract: This work presents a new insight into the potential of a Ni/CeZrO₂ catalyst in two separate processes: (i) Chemical Vapor Deposition (CVD) using methane as a feedstock to obtain carbon nanotubes (CNTs) and H₂, and (ii) catalyst regeneration with H₂O that yields H₂. The direct reaction of methane with H₂O (steam methane reforming (SMR)) leads to H₂ and CO (and CO₂), whereas carbon deposition—regardless of its type—is an unwanted reaction. The concept presented in this work assumes dividing that process into two reactors, which allows one to obtain two valuable products, i.e., CNTs and H₂. The literature data on CNT production via CVD ignores the issue of H₂ formation. Moreover, there is no data concerning CNT production in fluidized bed reactors over ceria-zirconia supported metal catalysts. The results presented in this work show that CNTs can be formed on Ni/CeZrO₂ during CH₄ decomposition, and that the catalyst can be easily regenerated with H₂O, which is accompanied by a high production of H₂. The ability of Ni/CeZrO₂ to be regenerated is its main advantage over the Ni-MgO catalyst that is popular for CNT production. This paper also shows that the Ni/CeZrO₂ catalyst has the potential to be used for CNT and H₂ production in a larger scale process, e.g., in a fluidized bed reactor.

Keywords: methane; hydrogen; CNTs; ceria-zirconia; nickel

1. Introduction

The demand for hydrogen has been increasing in the last decades, not only because it is a component of synthesis gas and used in the hydrogenation processes, but also because it is a perfect energy carrier, e.g., in fuel cells (FC). It is predicted that, in the short term, the request for hydrogen production will continue to increase [1]. The cheapest option of H₂ production is coal gasification, but the purification of raw gas for FC application is a great challenge, whereas H₂ production from renewable sources has been considered to be economically justified only since the second half of the 21st century [2,3]. From the perspective of sustainability, there is a need to switch from fossils to renewable sources and raw waste materials. The ideal source of hydrogen is water. So far, water photo-splitting, photo-reforming, and water electrolysis [4–7] have been proposed. The great advantage of these methods is that they are environmentally friendly. However, in the short-term, they are often far from practical (water-splitting is still in the initial phase of development). Currently, approximately 85% of the total hydrogen is produced via the steam reforming of natural gas. Obtained gas, besides H₂, also contains CO and CO₂; therefore, this hydrogen cannot be used straight away as a fuel in fuel cells because it would poison Pt-based anodes. Hence, the gas for FC application requires purification of CO. The oxidation of CO to CO₂ can be achieved, e.g., via a water gas shift (WGS) reaction (that also yields H₂) or preferential CO oxidation (PROX).

Another reaction (besides the steam reforming of methane or WGS) that produces hydrogen is the decomposition of methane. This option allows one to obtain pure hydrogen without CO or CO₂ emissions, since no oxidant, such as steam or oxygen, is used. Another advantage of this process
is the possibility of the formation of structural carbon deposits, such as carbon nanotubes (CNTs). This can be achieved only if the process is carried out over a proper catalyst. Carbon nanotubes have attracted considerable attention due to their outstanding physical and chemical properties. Multi-walled (MWNT) or single-walled carbon nanotubes (SWNT) are expected to cause a significant breakthrough in electronics and engineering materials [8,9]. Various methods of CNT synthesis have been developed. High-quality CNTs can be synthesized by laser vaporization [10] and electric arc discharge [11], but these methods are not adaptable to industrial CNT production. Chemical vapor deposition (CVD) [12–15] is the most promising method for the large-scale production of CNTs. CVD requires a lower temperature of reaction and lower cost [16]. Currently, the critical problem for the commercial applications of CNTs is their large-scale production. The price of CNTs is high, and has recently decreased, but is still excessive for realistic industrialization.

The most popular catalysts utilized in CNT formation via the CVD method are Fe, Co, Mo, and Ni, supported on MgO, SiO$_2$, Al$_2$O$_3$, CaO, and ZrO$_2$ [17–20]. Nickel catalysts were found to be very active and stable. Moreover, they work in a wide range of temperatures [21,22]. The most popular support used in the CVD process is MgO, which presents some advantage over other supports. For example, MgO can be removed within a mildly acidic environment without damaging the CNTs [23].

The most common processes for the CVD growth of CNTs are fixed bed, floating catalyst, and fluidized bed [24]. Among these three methods, the most promising is the fluidized bed, which provides a sufficient growing space for CNTs, as well as proper mass and heat transfer, leading to a greater yield and a higher quality of obtained CNTs [25]. Many researchers prefer to produce CNTs on a large scale by utilizing fluidized bed reactors [26–34]. Some companies have even commercialized CNT production with a fluidized bed process [35]. However, all the products of the present fluidized bed process are agglomerated CNT products. Vertically aligned CNTs have been obtained in a fluidized bed reactor by Zhang et al. [31]. Maghsoodi et al. [25] have studied the continuous production of CNTs via the CVD of methane over the Fe/MgO catalyst in a fluidized bed reactor at 900 °C. They obtained MWNTs of about 20 nm in size, as well as SWNTs of 1.0–1.2 nm in diameter. Corrias et al. [27] proved the high efficiency of the CVD fluidized bed process to manufacture CNTs. They obtained a carbon yield of over 95%, with selectivity to CNTs close to 100%. Hsieh et al. [28] investigated the production of high-quality CNTs over Fe and Ni-Al$_2$O$_3$ mixture catalysts in the reaction decomposition of acetylene in a fluidized bed reactor at 700–850 °C. Compared to CNTs grown in a fixed bed reactor, the CNTs produced in a fluidized bed reactor showed higher purity. Their observations revealed that fluidization is an essential factor in the growth process of well-defined CNTs. The activity of the Fe–Al$_2$O$_3$ catalyst was found to be higher than that of the Ni–Al$_2$O$_3$ catalyst. All presented research focuses on CNT production, disregarding the issue of hydrogen formation and its further processing.

There is no data about the production of CNTs in fluidized bed reactors over ceria-zirconia supported metal catalysts. In general, these catalysts are known for being resistant to carbon deposition. Metal supported CeZrO$_2$ catalysts are known for their high activity, e.g., in reforming reactions or WGS [36–38]. As studied in this work, a Ni catalyst supported on a commercial ceria-zirconia has already been found active in the steam reforming of toluene and 1-methylnaphthalene [39,40], and WGS. In specific conditions, the catalyst does not lose its activity, despite some carbon deposition. Moreover, owing to its high oxygen storage capacity (OSC), high oxygen mobility, and excellent redox properties of ceria-zirconia, the catalyst is able to dissociatively adsorb H$_2$O, providing very high hydrogen production. Some experiments of CH$_4$ decomposition and H$_2$O dissociation on powder Ni/CeZrO$_2$ have already been performed [41]. Hybrids materials composed of CNTs and Ni/CeZrO$_2$ have shown a good performance in the WGS reaction [42].

Hence, it is interesting to use a Ni/CeZrO$_2$ catalyst to (i) produce CNTs and hydrogen via CVD using methane as a feedstock, and afterward (ii) to regenerate the spent catalyst with H$_2$O with a simultaneous production of H$_2$. Presented in this work, mechanistic studies of these reactions, conducted by tests on a laboratory scale using a “micro-reactor”, have shown the potential of Ni/CeZrO$_2$ for further applications in fluidized bed reactors.
2. Experimental

2.1. Preparation of the Formed Ni/CeZrO₂ Catalyst

The CeZrO₂ powder (ACTALYS 921, Rhodia Catalyst, France), having the $S_{\text{BET}} = 180 \text{ m}^2/\text{g}$ and containing 68% of Ce and 32% of Zr, was formed in pellets ($W \times H = 5 \text{ mm} \times 4 \text{ mm}$) with the addition of 2 wt.% of graphite. The yellow CeZrO₂ pellets ($S_{\text{BET}} = 110 \text{ m}^2/\text{g}$) were impregnated with Ni(NO₃)₂·6H₂O aqueous solution, dried in two steps (at room temperature overnight and 120 °C for 12 h) and calcined at 700 °C for 5 h (Figure 1). The nominal Ni loading in the pellets was 10 wt.%. The obtained Ni/CeZrO₂ was then crushed and sieved to obtain a 0.125–0.2 mm fraction that was used for the further characterization and testing of CH₄ decomposition.

The Ni-MgO catalyst (used as a reference catalyst in this work) was obtained using the sol-gel method. Nickel and magnesium nitrates (Ni(NO₃)₂·6H₂O and Mg(NO₃)₂·6H₂O) were dissolved with citric acid in deionized water and stirred at room temperature for 24 h. Obtained green sol was heated at 70 °C until it transformed into a gel which was then dried at 120 °C overnight. Next, the resulting green foam was calcined at 700 °C for 5 h to obtain a light brown powder. In the next step, the Ni-MgO solid solution was formed under the pressure of 40 Kp/cm and crushed in a mortar to obtain a fraction of 0.125–0.2 mm. The Ni content in the catalyst was 43 wt.%.

2.2. Tests of CH₄ Decomposition and Catalyst Regeneration in H₂O

A series of tests of CH₄ decomposition over Ni/CeZrO₂ and Ni-MgO catalysts was performed in a quartz reactor of 1.2 cm diameter that was placed in an oven with T regulator (Figure 1). Catalyst samples were subjected to tests of (i) CH₄ decomposition of CNTs and H₂, and (ii) subsequent regeneration in H₂O. Both types of tests were conducted in temperature programmed (TP) conditions, raising the temperature from RT (for CH₄ decomposition) or 100 °C (for catalyst regeneration in H₂O) to 900 °C, with a heating rate of 10 °C/min. Tests of CH₄ decomposition on Ni/CeZrO₂ and Ni-MgO were performed in a flowing 2 vol.% CH₄/Ar and at a gas hourly space velocity (GHSV) of 7000 h⁻¹. Prior to some experiments, the catalyst was reduced by 5 vol.% H₂/Ar at 700 °C for 2 h. The Ni/CeZrO₂ was also subjected to tests in steady-state conditions in flowing 2 and 10 vol.% CH₄/Ar and GHSV = 7000 and 13,000 h⁻¹. Regeneration of catalysts was carried out in flowing
2.8 vol.% H₂O/Ar at GHSV = 5000 h⁻¹. The inlet and outlet gas composition were determined using a gas chromatograph equipped with a TCD.

2.3. Catalyst Characterization

The crystal structures of the Ni/CeZrO₂ and Ni-MgO catalysts were determined by a powder XRD diffractometer using Panalytical X’Pert Pro, Co-Kα radiation (λ = 0.1789 nm) and a Siemens 500D diffractometer employing Cu-Kα radiation (λ = 0.154 nm), respectively. The crystallographic structures of the samples and Miller indices (hkl) of the diffraction lines were determined using bibliographic data (JCPDS published by the Joint Committee on Powder Diffraction Standards). Thermogravimetric analyses of spent Ni/CeZrO₂ and Ni-MgO catalysts were performed using a Metter-Toledo apparatus. Analyses were conducted in flowing air with a linear temperature increase from RT to 950 °C with a heating rate of 10 °C/min. Scanning electron microscopy of Ni/CeZrO₂ was performed using the Quanta 250 FEG microscope. The micrographs were obtained under a low vacuum (80 Pa) with an acceleration voltage of 10 kV from secondary electrons collected by Large Filed Detector (LFD). High-resolution transmission electron microscopy (HRTEM) of Ni/CeZrO₂ was performed using the JEOL-JEM 2011 HR apparatus associated with a top entry device operating at 200 kV. The specific surface area (SSA) of Ni/CeZrO₂ was measured using the Quantachrome Autosorb iQ by physical adsorption of N₂ at the temperature of liquid nitrogen. The SSA was determined using the Brunauer-Emmett-Teller (BET) equation. Prior to measurements, samples were outgassed in a vacuum at 150 °C for 12 h.

3. Results and Discussion

3.1. CH₄ Decomposition to CNTs and H₂

The tests of CH₄ decomposition in temperature-programmed (TP) mode were carried out over unreduced and pre-reduced Ni/CeZrO₂ and Ni-MgO catalysts to determine the temperature region at which those reactions can occur. For determining the time needed either for optimal CNT production or catalyst regeneration, tests in isothermal conditions were performed. Figure 2 shows the evolution of CH₄, CO, CO₂, and H₂ as a function of temperature during methane decomposition. It can be seen that temperature profiles for unreduced and pre-reduced Ni/CeZrO₂ differ from each other. The decomposition of CH₄ is a few-step dehydrogenation, which requires the presence of reduced metal sites. Hence, as is seen in Figure 2a, the NiO in unreduced Ni/CeZrO₂ first undergoes reduction to Ni with CH₄ (evidenced by CO₂ formation from 580 °C; Equation (1)). Immediately after, methane dehydrogenates to release H₂ and form carbon species on Ni sites (Equation (2)). However, ceria-zirconia, owing to its high oxygen content and high oxygen mobility, is able to oxidize hydrocarbons to CO₂ and H₂O. Thus, the release of CO₂ to the gas phase can be partly ascribed to the reduction of CeZrO₂ (Equation (3)). The presence of CO in the gas phase could be due to the partial oxidation of CH₄ by the lattice oxygen from the ceria-zirconia (Equation (4)) or oxidation of the carbon species deposited on the Ni (Equation (5)). As presented in Figure 2b, the pre-reduction of Ni/CeZrO₂ allows the temperature of the methane dehydrogenation on Ni (Equation (6)) to significantly decrease as low as 200 °C, where H₂ formation starts. The reduction of CeZrO₂ with H₂ is only partial (Equation (7)). Therefore, the oxygen remaining in the lattice can still be used either for CH₄ or C oxidation to CO (Equations (4) and (5)), which is observed in the gas phase from 400 °C.

\[
4\text{NiO} + \text{CH}_4 = 4\text{Ni} + \text{CO}_2 + 2\text{H}_2\text{O} \quad (1)
\]

\[
\text{CH}_4 + \text{Ni} \rightarrow \text{Ni}(C) + 2\text{H}_2 \quad (2)
\]

\[
2\text{CeZrO}_2 + x\text{CH}_4 = 2\text{CeZrO}_{(2−2x)} + x\text{CO}_2 + 2x\text{H}_2\text{O} \quad (3)
\]

\[
\text{CeZrO}_2 + x\text{CH}_4 = \text{CeZrO}_{(2−x)} + x\text{CO} + 2x\text{H}_2 \quad (4)
\]
whereas CH (denoted Ni(C)). Catalyst pre-reduction allows the immediate dehydrogenation of CH. This process is why no, or insignificant, CO2 is formed during tests on pre-reduced Ni/CeZrO2 (Figure 4). The decomposition of CH4 on Ni-MgO takes place at higher temperatures than in cases of Ni/CeZrO2. Moreover, as can be seen in Figure 2c,d, catalyst pre-reduction does not have a significant impact on its performance. In both unreduced and reduced Ni-MgO, dehydrogenation of CH4 occurred from ca. 690 °C. Insignificant production of CO2 was observed on unreduced Ni-MgO at 690 °C.

The results of tests carried out over unreduced and pre-reduced Ni/CeZrO2 at 700 °C in flowing 2 and 10 vol.% CH4/Ar and at GHSV = 7000 and 13,000 h−1 are presented in Figures 3 and 4, whereas CH4 conversions and H2 yields for both forms of the catalyst are presented in Figures 5 and 6. As previously mentioned, CH4 decomposition over unreduced Ni/CeZrO2 is preceded by a reduction of NiO to zero-valent Ni. That is the reason for significant CO2 production from the beginning of the test on the unreduced catalyst (Figure 3). The presence of reduced metal sites allows hydrocarbon adsorption and its subsequent dehydrogenation, which manifests itself in H2 production that increases with the time of the experiment. At the same time, carbon deposits are formed on Ni (denoted Ni(C)). Catalyst pre-reduction allows the immediate dehydrogenation of CH4. This process is why no, or insignificant, CO2 is formed during tests on pre-reduced Ni/CeZrO2 (Figure 4).

\[
\text{CeZrO}_2 + \text{Ni(C)} = \text{CeZrO}_{2-\delta} + x\text{CO} + \text{Ni} \quad (5)
\]

\[
\text{NiO} + \text{H}_2 = \text{Ni} + \text{H}_2\text{O} \quad (6)
\]

\[
\text{CeZrO}_2 + x\text{H}_2 = \text{CeZrO}_{2-\delta} + x\text{H}_2\text{O} \quad (7)
\]
conversion and H₂ yield at different GHSVs was more visible during tests carried out under flowing 10 vol.% CH₄/Ar. The performance of unreduced Ni/CeZrO₂ was better when the GHSV was lower. It can be seen in Figure 3 that a lower GHSV (higher contact time) facilitates the oxidation of surface carbon species deposited on Ni, reactivating the same active sites for CH₄ dehydrogenation. The impact of GHSV on catalyst performance was insignificant for the pre-reduced Ni/CeZrO₂.

**Figure 3.** Gas composition at reactor outlet during tests of CH₄ decomposition on unreduced Ni/CeZrO₂ at gas hourly space velocity (GHSV) = 7000 h⁻¹ (a,b) and 13,000 h⁻¹ (c,d). Reaction mixture: 2 vol.% CH₄/Ar (a,c) and 10 vol.% CH₄/Ar (b,d).

**Figure 4.** Gas composition at reactor outlet during tests of CH₄ decomposition on pre-reduced Ni/CeZrO₂ at GHSV = 7000 h⁻¹ (a,b) and 13,000 h⁻¹ (c,d). Reaction mixture: 2 vol.% CH₄/Ar (a,c) and 10 vol.% CH₄/Ar (b,d).

The presented results indicate that significantly better results in terms of CH₄ conversion are obtained for low concentrations of methane in the reaction mixture (i.e., 2 vol.% CH₄/Ar). Pre-reduced or not, the Ni/CeZrO₂ does not contain a sufficient number of active sites for the complete conversion of CH₄ when its concentration in the feed is 10 vol.%. Moreover, it does not matter, from the perspective of methane conversion and H₂ yield, whether the catalyst was pre-reduced or not. In both cases,
100% CH$_4$ conversion and 100% H$_2$ yield were achieved after 1 h in flowing 2 vol.% CH$_4$/Ar at GHSV = 7000 h$^{-1}$. The increase of GHSV to 13,000 h$^{-1}$ resulted in a slight decrease (to ca. 90%) of methane conversion and H$_2$ yield. However, H$_2$ formation on the unreduced Ni/ CeZrO$_2$ stabilized after approximately 30 minutes, because at the beginning of the test the catalyst surface was being reduced, and the active sites for CH$_4$ dehydrogenation were just being formed. The difference in CH$_4$ conversion and H$_2$ yield at different GHSV's was more visible during tests carried out under flowing 10 vol.% CH$_4$/Ar. The performance of unreduced Ni/ CeZrO$_2$ was better when the GHSV was lower. It can be seen in Figure 3 that a lower GHSV (higher contact time) facilitates the oxidation of surface carbon species deposited on Ni, renovating the same active sites for CH$_4$ dehydrogenation. The impact of GHSV on catalyst performance was insignificant for the pre-reduced Ni/ CeZrO$_2$.

The increase in the catalyst mass after the above-described tests is presented in Table 1. Carbon deposition on Ni/ CeZrO$_2$ after a 1 h test in flowing 2 vol.% CH$_4$/Ar was very small: up to 2.5% for the unreduced catalyst and up to 3.6% for the pre-reduced one. Higher amounts of carbon deposits were noticed after tests carried out in flowing 10 vol.% CH$_4$/Ar. The maximal, but not satisfactory, mass increase that resulted from carbon deposition was noticed for pre-reduced Ni/ CeZrO$_2$ after a test carried out under GHSV = 7000 h$^{-1}$. In general, a higher number of active sites for CH$_4$ decomposition will lead to a higher amount of carbon deposits, but a study performed on powder Ni/ CeZrO$_2$ with Ni loading of 10 and 30 wt.% did not show significantly higher carbon build-up on the catalyst surface.

<table>
<thead>
<tr>
<th>Catalyst CH$_4$ (vol.%) GHSV (h$^{-1}$)</th>
<th>Carbon content (%)</th>
<th>CO yield (%)</th>
<th>H$_2$ yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unreduced 2 7000 2.1 1.1</td>
<td>26</td>
<td>3.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Pre-reduced 2 7000 3.6 1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-reduced 10 13,000 8.8 4.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-reduced 10 7000 9.0 4.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-reduced 2 13,000 3.1 1.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The initial state of the catalyst (unreduced or pre-reduced) has an impact on the CO and CO$_2$ presence in the product gas. It is obvious that the presence of CO$_2$ in the gas phase is due to catalyst reduction by methane, which is the reason for its absence during tests on the pre-reduced catalyst. CO is produced on both catalysts, but is significantly higher on the unreduced one because of a higher content of oxygen in the ceria-zirconia lattice. As mentioned before, oxygen can oxidize either CH$_4$ or carbon species deposited on Ni (Equations (4) and (5)).

![Figure 5. CH$_4$ conversion (a) and H$_2$ yield (b) during tests carried out on unreduced Ni/ CeZrO$_2$ in flowing 2 and 10 vol.% CH$_4$/Ar, and at GHSV = 7000 and 13,000 h$^{-1}$.](image)

![Figure 6. CH$_4$ conversion (a) and H$_2$ yield (b) during tests carried out on pre-reduced Ni/ CeZrO$_2$ in flowing 2 and 10 vol.% CH$_4$/Ar, and at GHSV = 7000 and 13,000 h$^{-1}$.](image)
(Table S1). At such a high metal loading, Ni particles formed large agglomerates; thus, the number of Ni particles accessible for CH₄ adsorption and dehydrogenation was lower than expected.

**Table 1.** Increase in Ni/CeZrO₂ mass after tests of CH₄ decomposition (T = 700 °C; t = 1 h).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CH₄ (vol.%)</th>
<th>GHSV (h⁻¹)</th>
<th>Δm (%)</th>
<th>C/Ni (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>unreduced</td>
<td>2</td>
<td>7000</td>
<td>2.1</td>
<td>1.1</td>
</tr>
<tr>
<td>unreduced</td>
<td>2</td>
<td>13,000</td>
<td>2.5</td>
<td>1.3</td>
</tr>
<tr>
<td>unreduced</td>
<td>10</td>
<td>7000</td>
<td>8.3</td>
<td>4.5</td>
</tr>
<tr>
<td>unreduced</td>
<td>10</td>
<td>13,000</td>
<td>7.9</td>
<td>4.2</td>
</tr>
<tr>
<td>pre-reduced</td>
<td>2</td>
<td>7000</td>
<td>3.6</td>
<td>1.9</td>
</tr>
<tr>
<td>pre-reduced</td>
<td>2</td>
<td>13,000</td>
<td>3.1</td>
<td>1.7</td>
</tr>
<tr>
<td>pre-reduced</td>
<td>10</td>
<td>7000</td>
<td>8.8</td>
<td>4.7</td>
</tr>
</tbody>
</table>

Thermogravimetric analysis of the unreduced Ni/CeZrO₂ after a 1 h test of CH₄ decomposition carried out in flowing 10 vol.% CH₄/Ar at GHSV = 7000 h⁻¹ (Figure 7a) showed a 12% mass decrease, of which 8.3% was carbon deposits. The sample contained about 2.8% of amorphous carbon (DTG, negative peak at 400 °C) and 5.5% of structural carbon (negative peak at 600 °C). On the contrary, the TGA for Ni-MgO after CH₄ decomposition at the same conditions revealed that carbon content in the sample was as high as 79% (which corresponds to 8.9 mol C/mol Ni—over 2 times higher than for Ni/CeZrO₂). Deposited carbon was in most structural (peak at 715 °C on the DTG curve in Figure 7b).

![Figure 7. TGA for (a) Ni/CeZrO₂ and (b) Ni-MgO catalyst after CH₄ decomposition (T = 700 °C; 10 vol.% CH₄/Ar; GHSV = 7000 h⁻¹; t = 1 h).](image)

The XRD of Ni/CeZrO₂ and Ni-MgO catalysts are presented in Figure 8. Typical reflections for the CeZrO₂ phase can be observed on diffractograms for pristine CeZrO₂ (Figure S1), and fresh and spent Ni/CeZrO₂ catalysts (Figure 8a). The presence of NiO in the fresh catalyst (curve “i”), as well as its reduction to Ni (curve “ii”), is proven by the appearance of reflections at ca. 43, 51, and 75° (NiO) and 52 and 61° (Ni). No reflections indicating the presence of structural carbon (CNTs) can be observed at ca. 26°, which is due to its very low content in the sample. The diffractogram of fresh Ni-MgO (Figure 8b, curve “i”) displays only peaks characteristic of the solid Ni-MgO solution. The reduction of the catalyst in flowing H₂ and CH₄ led to the formation of Ni phase (peaks at ca. 45, 52, and 74°); however, the Ni-MgO phase was still occurring. Unlike the case of Ni/CeZrO₂, the diffractogram of the Ni-MgO catalyst after CH₄ decomposition displayed a peak at ca. 26°, thereby providing the evidence for the presence of structural carbon deposits.
The SEM observations of the Ni/CeZrO$_2$ catalyst before and after CH$_4$ decomposition are presented in Figure 9. Due to the low carbon amount in the sample after 1 h tests, it was impossible to detect carbon using SEM. In order to determine particular types of carbon species on the catalyst surface after CH$_4$ decomposition, the SEM observations were performed for the catalyst sample after 3 h of CH$_4$ decomposition. As presented in Figure 9b, some grains of Ni/CeZrO$_2$ were covered with filamentous carbon deposits. However, those covered with carbon deposit grains were detected only in the same regions of the sample, whilst most of the catalyst particles remained unaffected. The SEM analysis revealed the presence of filamentous carbon of different curvatures and lengths (Figure 9c,d), whereas TEM (Figure 10) proved that these were CNTs (the presence of parallel graphene layers). The external diameters of detected multiwall CNTs were up to 64 nm. It was also observed that Ni/CeZrO$_2$ nanoparticles were attached to CNT walls. Those in situ formed hybrid materials (i.e., Ni/CeZrO$_2$@CNT) can reveal catalytic activity, e.g., in water gas shift [42] or methane dry reforming (Figure S2).

Figure 8. XRD for (a) Ni/CeZrO$_2$ and (b) Ni-MgO: (i) fresh, (ii) pre-reduced in H$_2$, (iii) after CH$_4$ decomposition, (iv) after subsequent regeneration with H$_2$O. The peaks of the CeZrO$_2$ phase in (a) were denoted “CZ”.

Figure 9. SEM of Ni/CeZrO$_2$ (a) before and (b–d) after CH$_4$ decomposition at T = 700 °C under flowing 10 vol.% CH$_4$/Ar for t = 3 h.
Figure 9. SEM of Ni/CeZrO$_2$ (a) before and (b–d) after CH$_4$ decomposition at T = 700 °C under flowing 10 vol.% CH$_4$/Ar for t = 3 h.

Figure 10. TEM of Ni/CeZrO$_2$ catalyst after CH$_4$ decomposition at T = 700 °C under flowing 10 vol.% CH$_4$/Ar for t = 3 h.

The Ni/CeZrO$_2$ catalyst was also subjected to N$_2$ sorption in order to determine its textural properties. The specific surface area (SSA), pore volume, and mean pore size are presented in Table 2. It can be observed that the textural properties of the catalyst did not change after its reduction in H$_2$. However, the increase of specific surface area can be observed for the Ni/CeZrO$_2$ sample spent in CH$_4$ decomposition. The increase in SSA, as well as the decrease in mean pore size, can be explained by the presence of CNTs in the sample (also proven by TGA and microscopic observations).

Table 2. Textural properties of fresh, spent, and regenerated Ni/CeZrO$_2$.

<table>
<thead>
<tr>
<th>Ni/CeZrO$_2$:</th>
<th>SSA (m$^2$/g)</th>
<th>Pore Volume (cc/g)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>fresh</td>
<td>78</td>
<td>0.25</td>
<td>13.2</td>
</tr>
<tr>
<td>pre-reduced in H$_2$</td>
<td>74</td>
<td>0.25</td>
<td>13.1</td>
</tr>
<tr>
<td>after CH$_4$ decomposition</td>
<td>83</td>
<td>0.26</td>
<td>11.4</td>
</tr>
<tr>
<td>regenerated in H$_2$O **</td>
<td>95</td>
<td>0.28</td>
<td>13.1</td>
</tr>
</tbody>
</table>

* 10 vol.% CH$_4$/Ar; 700 °C/3 h; GHSV = 7000 h$^{-1}$, ** 2.8 vol.% H$_2$O/Ar; 650 °C.

3.2. Catalyst Regeneration with H$_2$O

The samples of Ni/CeZrO$_2$ and Ni-MgO spent in the reaction of CH$_4$ decomposition at 700 °C were subjected to treatment with flowing 2.8 vol.% H$_2$O/Ar in temperature programmed conditions and in isotherms. These tests aimed at determining the optimal temperature of catalyst regeneration with H$_2$ production.

The temperature profile of Ni/CeZrO$_2$ regeneration with H$_2$O is presented in Figure 11a. It reveals that carbon deposits present on catalyst surface are oxidized with a significant production of H$_2$ from ca. 500 °C; however even at lower temperatures some oxidation takes place. The formation of CO$_2$ is observed from temperatures as low as 150 °C. The presence of CO$_2$, the gas phase, at low temperatures may be due to the desorption of carbonates from the CeZrO$_2$ surface, which is followed with the formation of oxygen vacancies (*) that are active sites (e.g., for the adsorption and dissociation of H$_2$O (Equation (8)). Hydrogen release to the gas phase is observed from 250 °C. Beside oxygen vacancies, H$_2$O dissociates on Ni sites (also denoted “**” in Equation (8)). Oxygen species (O*) adsorbed on catalyst surfaces as a result of H$_2$O dissociation are used for the oxidation of reactive carbon species (*C) to CO$_2$ (Equations (9)–(11)). The ability of ceria-zirconia support to oxidize carbon deposits
on Ni/CeZrO₂ using lattice oxygen has been proven by an experiment carried out in flowing Ar (Figure S3). The most reactive carbon deposits are oxidized first, i.e., the amorphous carbon is oxidized up to ca. 500 °C, whereas CNTs are oxidized above this temperature. From ca. 500 °C, a significant increase in H₂ and CO₂ formation is observed.

\[
\begin{align*}
H_2O + * &= O^* + H_2 \\
C^* + O^* &= CO^* + * \\
CO^* &= CO + * \\
CO + O^* &= CO_2 + * \\
H_2O + Ni &= NiO + H_2
\end{align*}
\]

Figure 11b–d present the evolution of H₂, CO, and CO₂ as a function of time during catalyst regeneration at three temperatures: (i) at 420 °C, because there is no CO formation on TP profile, (ii) at 550 °C, which is the temperature of maximal H₂ formation, and (iii) at 650 °C, where CO formation dominates over CO₂ production.

![Figure 11](image-url)

**Figure 11.** Regeneration of Ni/CeZrO₂ in 2.8 vol.% H₂O/Ar in (a) temperature programmed conditions, and at (b) 420 °C, (c) 550 °C and (d) 650 °C.

The regeneration of Ni/CeZrO₂ at 420 °C takes place slowly and with low H₂ and CO₂ formation. Carbon species oxidize mainly to CO₂, but some CO production is also observed. Maximal conversion of H₂O to H₂ is 30%. After oxidation of the surface carbon species (i.e., after 9 h of regeneration, where neither CO₂ nor CO is observed in the gas phase) H₂O oxidizes Ni to NiO, which yields pure H₂ (Equation (12)). The conversion of H₂O is only 0.9% because the rate of Ni oxidation is low, whereas, catalyst regeneration at 550 °C is faster and allowed almost 100% H₂O conversion during the first 2 h of the test run. The oxidation of the carbon deposits takes place with the formation of H₂, CO₂, and CO. The most significant production of H₂, CO₂, and CO occurs in the first hours. At that time, the most reactive carbon deposits are oxidized. Simultaneously, structural carbon (CNTs) is oxidized,
but because it is less reactive, its removal with H$_2$O requires more time. After 5 h of the test run, no CO$_2$ and CO is observed in the gas phase, and only H$_2$ formation is noticed. The oxidation of Ni to NiO at 550 °C occurs faster than at 420 °C; therefore, H$_2$O conversion is also higher (7% from the fifth hour of the test run). During catalyst regeneration at 650 °C, the formation of CO dominates over CO$_2$. Hydrogen production is very high—almost 100% of H$_2$O is converted in the first 2 h of the test run and then decreases due to the reduction of carbon deposits. Total removal of the deposits at 650 °C is reached after 8 h of the test run.

To summarize, catalyst regeneration at 420 °C allows oxidizing only reactive, amorphous carbon deposits. It also produces the lowest amount of CO. Regeneration carried out at 550 and 650 °C yields almost 100% H$_2$O conversion in the first 2 h of the test run, later it decreases. More CO$_2$ is produced during regeneration at 550 °C, while the process carried out at 650 °C leads mainly to CO (except for H$_2$, whose production is the most important). Regeneration of Ni/CeZrO$_2$ at 550 °C seemed to be finished after 5 h (no CO$_2$ and CO detected in the gas phase), while the process carried out at 650 °C led mainly to CO (except for H$_2$, whose production was the most important). The shorter time of carbon deposits oxidation at 550 °C indicates that not all deposits were removed from the catalyst; 550 °C is probably too low for oxidation of the least reactive structural carbon deposits. The most resistant to oxidation with H$_2$O are probably the CNTs that had the loosest contact with the Ni/CeZrO$_2$ catalyst. Complete regeneration and re-oxidation of Ni/CeZrO$_2$ was achieved only at 650 °C. After that regeneration test, the catalyst changed its color from black (after CH$_4$ decomposition) to green-grey, as presented in Figure 1. The XRD analysis (Figure 8a, curve “iv”) also proved the regeneration of Ni/CeZrO$_2$ and re-oxidation of Ni to NiO.

Hydrogen production during the regeneration of Ni/CeZrO$_2$ with H$_2$O was very high—higher than the hydrogen production arising from the oxidation of carbon deposits to CO and/or CO$_2$. For producing 1 mole of CO, 1 mole of H$_2$O is required (Equation (17); elementary steps are described by Equations (13) and (14)). However, to produce 1 mole of CO$_2$, 2 moles of H$_2$O are needed (Equation (16); elementary steps described by Equations (13), (14) and (15)). Knowing the composition of the gas mixture at the outlet of reactor, we can calculate how much H$_2$ was produced in each reaction. However, looking at the H$_2$/(CO + CO$_2$) ratio during regeneration tests at 420, 550, and 650 °C (Figure 12), it can be noticed that this ratio was higher than its maximal theoretical value, i.e., 2 (Equation (16); assuming that all CO is converted to CO$_2$). Hence, the formation of H$_2$ that is not linked to CO or CO$_2$ production (Equations (16) and (17)) indicates its overproduction owing to H$_2$O dissociation on (i) oxygen vacancies of CeZrO$_2$ that lead to re-oxidation of Ce$^{3+}$ to Ce$^{4+}$, and (ii) zero-valent Ni (Equation (12)) that leads to NiO.

\[
2\text{H}_2\text{O} + 2* = 2\text{H}_2 + 2\text{O}^* \quad (13)
\]
\[
\text{C} + \text{O}^* = \text{CO} + * \quad (14)
\]
\[
\text{CO} + \text{O}^* = \text{CO}_2 + * \quad (15)
\]
\[
2\text{H}_2\text{O} + \text{C} = 2\text{H}_2 + \text{CO}_2 \quad \text{H}_2/(\text{CO} + \text{CO}_2) = 2 \quad (16)
\]
\[
\text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2 \quad (17)
\]
The results of regeneration tests for Ni-MgO are presented in Figure 13. The temperature profile for catalyst regeneration after CH$_4$ decomposition (Figure 13a) shows that carbon deposits are oxidized from 600 °C, which manifests itself with CO$_2$ formation, followed by H$_2$ desorption to the gas phase. The formation of CO is observed from ca. 700 °C. Thus, regeneration of Ni-MgO with H$_2$O requires higher temperatures than the regeneration of Ni/CeZrO$_2$. In the case of the Ni-MgO catalyst, only the Ni phase takes part in H$_2$O dissociation. The regeneration of Ni-MgO in isothermal conditions was performed at 700 °C. At this temperature, all carbon species deposited on the catalyst surface should be removed. It can be observed in Figure 13b that carbon deposits were oxidized with H$_2$O to CO$_2$, CO, and H$_2$ during the first 3.5 h of the test run. Later, only small amounts of CO and H$_2$ were detected. Finally, at the end of the process, only H$_2$ was formed, owing to the Ni re-oxidation to NiO. It was proven by XRD (Figure 8b, curve “iv”) that H$_2$O treatment at 700 °C removed carbon deposits from the catalyst (no reflection at ca. 26°); however, the Ni phase can still be observed on diffractogram, which shows that it was only partly re-oxidized to NiO.

![Figure 12. H$_2$/(CO + CO$_2$) ratio during regeneration of Ni/CeZrO$_2$ at 420 °C (▲), 550 °C (●) and 650 °C (◆), and Ni-MgO at 700 °C (×).](image)

**Figure 13.** Regeneration of Ni-MgO in 2.8 vol.% H$_2$O/Ar in (a) temperature programmed conditions and (b) at 700 °C.

### 4. Conclusions

In order to assess the potential of Ni/CeZrO$_2$ for CNTs and H$_2$ production in fluidized bed reactors, the formed (and crushed) catalyst was subjected to tests of CH$_4$ decomposition followed by regeneration with H$_2$O.

The decomposition of CH$_4$ to H$_2$ and carbon deposits occur from 580 °C on unreduced Ni/CeZrO$_2$ and from 200 °C on pre-reduced Ni/CeZrO$_2$. Catalyst pre-reduction significantly decreases the temperature of CH$_4$ dehydrogenation, due to the presence of zero-valent Ni. Nevertheless, catalyst pre-reduction is not important for the sake of H$_2$ production, which is the highest in the same temperature region as for unreduced catalyst, i.e., above 600 °C. Hence, the in-situ reduction of...
the Ni/CeZrO₂ catalyst with CH₄ is a reasonable solution (the process is more efficient because it does not waste valuable H₂).

It was found that very high CH₄ conversion and H₂ yield can be achieved during the decomposition of CH₄ at a low concentration in the feed (e.g., 2 vol.% in Ar). However, this process results in very low carbon deposition. An increase in CH₄ concentration in the feed results in higher carbon deposition on Ni/CeZrO₂, at the cost of CH₄ conversion and H₂ yield, which is caused by an insufficient number of Ni active sites.

The characterization of spent Ni/CeZrO₂ revealed that obtained carbon deposits comprised both the amorphous and structural carbon. The presence of CNTs was proven by TEM.

Regeneration of the Ni/CeZrO₂ catalyst with H₂O is possible from ca. 400 °C. At lower temperatures, H₂O oxidizes only the amorphous carbon species (at 420 °C) or CNTs that are in contact with Ni/CeZrO₂ particles (at 550 °C). Oxidation of all carbon deposits with H₂O, including the CNTs that detached from the catalyst particles, requires higher temperatures (e.g., 650 °C). Moreover, it was found that formation of H₂ during the regeneration of Ni/CeZrO₂ is not linked exclusively to carbon oxidation, but also comes from H₂O dissociation on (i) the oxygen vacancies of CeZrO₂ (re-oxidation of Ce³⁺ to Ce⁴⁺), and (ii) zero-valent Ni (re-oxidation to NiO). Complete regeneration of Ni/CeZrO₂ was achieved at 650 °C, which was proven by XRD.

Regeneration of the Ni-MgO catalyst occurs at higher temperatures than the regeneration of Ni/CeZrO₂. Carbon deposits were removed from Ni-MgO at 700 °C; however, the catalyst was not re-oxidized completely. Hydrogen production during Ni-MgO regeneration with H₂O comes only from the oxidation of carbon deposits and partial re-oxidation of the Ni phase.

The presented results show that the Ni/CeZrO₂ catalyst has the potential to be used for H₂ and CNT production using CH₄ and H₂O. The possibility of very high H₂ production is the main advantage of Ni/CeZrO₂ catalyst over Ni-MgO. The cognition of catalyst behavior was helpful for determining some parameters of CH₄ decomposition and catalyst regeneration in a fluidized bed reactor.

Supplementary Materials: The following are available online at http://www.mdpi.com/2305-7084/3/1/26/s1, Figure S1: XRD of CeZrO₂ support, Figure S2: CH₄ and CO₂ conversion during dry reforming of methane over Ni/CeZrO₂@CNT hybrid catalyst, Figure S3: Temperature profile for spent Ni/CeZrO₂ in flowing Ar, Table S1: Weight increase for powder Ni/CeZrO₂ after decomposition of 10 vol.% CH₄/Ar at 500, 600, and 700 °C for 3 h.

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