Article

Dry Reforming of Methane over CNT-Supported CeZrO₂, Ni and Ni-CeZrO₂ Catalysts

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Abstract: In this work, the carbon nanotubes (CNT)-supported nanosized, well-dispersed, CeZrO₂ and Ni-CeZrO₂ catalysts were obtained and tested for the first time in the reaction of methane dry reforming (DRM). The performance of the hybrid materials was compared with the performance of Ni/CNT catalyst. The mechanism of the DRM reaction and the occurrence of reverse water gas shift reaction (RWGS) and CO₂ deoxidation were discussed in terms of catalysts composition. The contribution of RWGS and CO₂ deoxidation in the DRM process, demonstrating an increased CO₂ consumption when compared to CH₄, and H₂/CO < 1, varied depending on the catalyst composition, was also studied.

Keywords: methane dry reforming; hydrogen; CNT; CO₂; ceria; CeZrO₂; Ni

1. Introduction

The climate change is one of the most important issues the modern society struggles with. The main foundation of this transformation is the growing atmospheric pollution caused by the greenhouse gases (GHGs), i.e., water vapor (H₂O), methane (CH₄), carbon dioxide (CO₂), fluorochlorocarbons and nitrous oxides (NO_x). The highest contribution to the increasing CO₂ and CH₄ emissions has the agricultural industry, coal- and natural gas-based industry, and transportation. It is estimated, that increasing demand for energy (still mainly produced from fossil fuels) has 80–85% contribution to global warming [1]. Several methods for GHGs conversion have been developed in order to reduce their negative impact on the environment. One of them is the dry reforming of methane (DRM) (Equation (1)), which allows conversion of two GHGs (CH₄ and CO₂) to a syngas (H₂ and CO), being a building block for various organic syntheses. Moreover, the DRM reaction can be also considered as a possible route for natural gas valorisation. The DRM reaction is accompanied by such side reactions as the Boudouard reaction (Equation (2)), the methane cracking (Equation (3)) and the reverse water–gas shift (Equation (4)) [2].

The DRM is a more endothermic process compared to other popular reactions allowing CH₄ conversion to syngas, i.e., the partial oxidation (POM) and steam reforming (SRM) [3]. Besides, compared to POM and SRM, the DRM is advantageous because it produces the syngas with the H₂/CO

ratio close to 1, which is proper for the production of liquid hydrocarbons via the Fischer–Tropsch synthesis of the dimethyl ether (DME) synthesis.

The DRM reaction requires temperatures as high as 800–1000 °C and is usually carried out over transition and noble metal-based catalysts; however, the most popular choice of the researchers in terms of catalyst active site is nickel, which is cheap and accessible. Other transition metals used for DRM, i.e., Fe and Co, are more prone to coking and thus the blockage of metallic active sites [4]. In general, the DRM reaction is at high risk of carbon deposition because it is thermodynamically favoured in the temperature window for DRM. According to Cao et al. [5], the decomposition of CH₄ to C and H₂ (Equation (3)) occurs from ca. 550 °C, whereas gasification of carbon deposit with CO₂ takes place above 700 °C. Therefore, carbon formation during DRM is the most detrimental for the catalyst from 550 to 700 °C. Moreover, the process of carbon deposition is more likely to occur on larger Ni crystallites [6]. Another problem occurring during DRM reaction is the sintering of the active phase resulting from the high temperature of the reaction. The thermodynamics of DRM process hinder its practical industrial application; therefore, the main focus of researchers dealing with that reaction is currently on improving the thermal stability of Ni-based catalysts and their resistance to coke formation. It can be achieved e.g., by creating the bimetallic structures, proper selection of the support or promoter, or changing the preparation method [7]. One of the key strategies is to design the catalysts containing the active metal site attached to the high-surface-area support (usually an oxide), remembering that the essential role in this system plays the metal-support interface. The strong metal-support interaction effect (SMSI) is the reason for improved performance of the catalyst and has been studied for over 60 years now [8]. The electron transfer between support and metal or metal oxide leads to profound changes in the chemisorption and catalytic properties of the catalyst as well as the morphology of the metal or metal oxide particles [9]. As was found by Kim et al. [10], improved catalytic activity in CO oxidation of the nanostructure of Pt–NiO_{1–x} supported on the bimetallic Pt₃Ni(111) originates from the SMSI effect that provides thermodynamically efficient reaction pathways. In the case of studied catalyst, the formation of interfacial Pt–NiO_{1–x} allowed lowering the heat of reaction on the surface. Therefore, it is important to provide such parameters of the catalyst synthesis, so that the interaction between metal site and the support was strong enough for good electron transfer between both phases, or the formation of the intermediate phases [11]. The Ni-based catalyst used for DRM are usually supported e.g., on Al₂O₃ [2,12,13], MgO [14], SiO₂ [15], CeO₂ [16,17], ZrO₂ [18], CeO₂–ZrO₂ [18–20], zeolites [21] and others, including carbonaceous materials [22,23].

The CNTs have been used as catalysts and supports many heterogeneous reactions, e.g., water gas shift (WGS) [24] or preferential CO oxidation (PROX) [25,26] or already mentioned DRM [22,23]. The chemical inertness of CNTs, their thermal resistance, developed surface area, mesoporous structure, uniform pore size distribution and high heat transfer, make them a good catalysts support [27]. Ma et al. [22] studied the performance of Ni nanoparticles dispersed selectively inside (I) or outside (O) carbon nanotubes. The CH₄ conversion in DRM over I–Ni/CNTs and r O–Ni/CNTs at 750 °C was 70 and 59%, respectively. The former was also more stable. Figueira et al. [23] studied the activity of Ce + Sr (or Ni) nanoparticles deposited inside the CNTs and Co (or Ni) nanoparticles anchored to the external CNT walls. According to their research, both the CeSr/MWCNT/Co and Ni/MWCNT/Ni catalyst showed high CO₂ and CH₄ conversions at 700 °C.

DRM reaction over Ni/CNT and Ni/SiO₂ was studied by Donphai et al. [28]. Both catalysts showed similar performance in terms of methane conversion, but Ni/CNT showed much better stability owing to carbon deposition along the CNT tips instead of the Ni sites. Khavarian et al. [29] reported that Co/CNT catalyst showed higher CH₄ conversions in DRM than Co/MgO, which was also attributed to lower rates of carbon deposition rates, and thus less catalyst deactivation, in the case of the former.

The cerium oxide (CeO₂) is a very attractive component of the support or promoter in catalytic systems used in DRM [30]. It is well-known for its high oxygen storage arising from easy transformation between 3+ and 4+ oxidation state. The high surface ceria was found very promising candidate catalyst for DRM owing to very high resistance towards carbon deposition and good thermal stability compared

to low surface area CeO_2 [31]. The addition of zirconium oxide (ZrO_2) promotes bulk reduction of CeO_2 - ZrO_2 -mixed oxide (denoted CeZrO_2). The redox ageing often leads to improved TPR behaviour at moderate temperatures, which implies high thermal stability and oxygen storage capacity in the CeZrO_2 . The catalysts supported on CeZrO_2 are more resistant to thermal ageing than those containing only CeO_2 . Moreover, the presence of Zr^{4+} shifts the temperature of Ce^{4+} reduction into lower values. Nevertheless, during the reduction of CeZrO_2 , only cerium is reduced from 4+ to 3+, while zirconium ions stay on +4 oxidation state [32]. It has been found that the thermodynamic properties of ceria-zirconia solid solutions differ dramatically from those of pure ceria [33]. Charisiou et al. [34] reported that alumina modified with CeO_2 (and La_2O_3) was more active and stable during biogas dry reforming than alumina alone. The increased activity in DRM of NiMoMgAl hydrotalcite-derived catalyst was noticed when it was promoted with CeZrO_2 [35]. The CeO_2 and CeZrO_2 -promoted or supported catalysts were tested in DRM by others [36–39]. Wolfbeisser et al. [18] reported that the synthesis method had a strong impact on the performance of Ni/ CeZrO_2 catalyst in DRM, whereas the composition of the catalyst had been of minor importance. Moreover, there was no significant difference between the activity of Ni/ CeZrO_2 and Ni/ ZrO_2 catalysts; however, the former was more resistant to the deposition of filamentous carbon species, which reduced the risk of reactor blocking. The positive effect of CeO_2 on catalyst resistance towards carbon deposition in DRM was also noticed by Mesrar et al. [40], who studied the activity of Ni/perlite catalysts. According to their research, the best performance revealed the CeO_2 /Ni/perlite containing 20 wt.% of ceria. The addition of CeO_2 to Ni-supported catalysts was found beneficial for the nickel dispersion, which improved the catalytic performance and reduced the coke formation on the catalyst surface [20,41–43]. The Ni- CeO_2 interaction was studied by Zhou et al. [44] using X-ray photoelectron spectroscopy (XPS) and scanning tunnelling microscopy (STM). It was found that redox properties of ceria and temperatures of Ni deposition over ceria, greatly influence the size, dispersion and electronic properties of Ni nanoparticles. However, Ni deposited on cerium oxides can agglomerate at high temperatures, resulting in decrease of catalyst activity [45]. At higher temperatures, owing to SMSI, new active sites can be formed on the Ni-ceria surface. Moreover, the charge transfer from Ni to CeO_2 allows Ni oxidation to Ni^{2+} with simultaneous reduction of Ce^{4+} to Ce^{3+} .

In this work we deal with CNT-supported Ni, CeZrO_2 and Ni- CeZrO_2 , and their potential application in DRM, whereas the two latter catalysts are for the first time examined in terms of their performance in this reaction. The addition of CeZrO_2 phase to the already known Ni/CNT catalyst aimed at reducing Ni deactivation caused by carbon deposition occurring during DRM. The dependence of DRM mechanism and the occurrence of RWGS and CO_2 deoxidation is discussed in respect of catalysts composition.

2. Results and Discussion

2.1. Characterization

The X-ray diffraction (XRD) patterns for functionalized CNTs (denoted CNT_{ox}), CeZrO_2 /CNT (denoted CZ/CNT), Ni CeZrO_2 /CNT (denoted NiCZ/CNT) and Ni/CNT catalysts are presented in Figure 1. The diffraction peak at ca. 26° visible for all samples is assigned to CNTs. Both the CZ/CNT and NiCZ/CNT diffractograms show reflexions at ca. 29.5 , 33.9 , 48.5 and 57.3° corresponding to (111), (200), (311) and (222) planes of CeZrO_2 , respectively.

For the Ni/CNT and NiCZ/CNT samples, the diffraction peaks located at ca. 44.6 and 51.9° are assigned to (111) and (200) planes of Ni, respectively. The NiO phase occurs only in Ni/CZ sample and it is detected by the reflexions at 37.5 , 43.5 and 63.0° corresponding to (101), (012) and (110) planes, respectively [46]. Hence, thermal decomposition of Ni(OH)_2 on CNT support, precipitated from $\text{Ni(NO}_3)_2$ using NaOH, can be followed with partial (in the case of Ni/CNT) and total (for NiCZ/CNT) reduction of NiO to Ni. The presence of both NiO and Ni on the CNT walls in Ni/CNT catalyst after its annealing was reported e.g., in [47,48]. In the case of NiCZ/CNT catalyst annealing leads to Ni (the NiO

phase is not detected by the XRD), and in this case, the total reduction of NiO to Ni can be caused by the strong contact between nickel phase and CeZrO₂. Since the annealing of NiCZ/CNT was carried out at 500 °C, some oxygen could desorb from CeZrO₂ crystal lattice, producing oxygen vacancies. The CeZrO₂ is well-known for high oxygen mobility and redox properties that could facilitate the transformation of Ni(OH)₂ to Ni.

Figure 1. XRD patterns of CNT_{ox}, CZ/CNT, NiCZ/CNT and Ni/CNT.

The morphologies of CNT-supported Ni, CeZrO₂ and Ni-CeZrO₂ are presented in Figures 2–4. The Ni and CeZrO₂ crystals display grey or white on the bright and dark field TEM pictures, respectively. The distribution of the active phase in the CZ/CNT catalyst is good. It was detected by the energy dispersive spectroscopy (EDS) that Ce and Zr occur in the same area indicating the formation of CeZrO₂. It can be seen in Figure 2c and d that the spherical particles of CeZrO₂ are well dispersed over CNT surface. It was determined that the size of CeZrO₂ crystallites varies from 1.21 to 4.22 nm, with 2.22 nm being the mean size. The histogram showing the size distribution of CeZrO₂ particle is presented in Figure 2b.

Figure 2. Bright field (a) and dark field (b,c) TEM pictures of CZ/CNT with CeZrO₂ particle size distribution (d).

Figure 3. Bright field (a) and dark field (b,c) TEM pictures of Ni/CNT with Ni particle size distribution (d).

Figure 4. Bright field (a) and dark field (b,c) TEM pictures of NiCeZrO₂/CNT with Ni-CeZrO₂ particle size distribution (d).

The dispersion of nickel phase on CNTs in Ni/CNT catalyst (Figure 3) is also good; however, the presence of two nickel fractions can be observed, i.e.: (i) small-size, spherical, non-agglomerated crystallites of the mean diameter close to 5 nm, and (ii) larger agglomerates whose size exceeds 15 nm.

Combination of both active phases, i.e., Ni and CeZrO₂ in NiCeZrO₂/CNT catalyst, also results in their good dispersion over the CNT support (Figure 4). It was detected by elemental mapping and selected area electron diffraction that Ni occurs in proximity to the Ce and Zr (Figure 5). This indicates strong contact between Ni and CeZrO₂. It was determined, that the size of Ni-CeZrO₂ particles varies from 1.06 to 3.46 nm, with a mean diameter of 2.11 nm (Figure 4b).

The N₂ adsorption/desorption isotherms for CNT-supported CeZrO₂, Ni and Ni-CeZrO₂ are shown in Figure 6, and they are similar to type IV isotherm according to IUPAC classification. The occurrence of hysteresis loop visible for all samples prove the existence of mesopores. The textural properties of all samples, i.e., the specific surface area (SSA), the total pore volume (V_t), the volumes of micro-, meso- and macropores, and the average pore size (d), are presented in Table 1. The CeZrO₂-containing catalysts (CZ/CNT and NiCZ/CNT) show significantly lower specific surface areas when compared to Ni/CNT, which can arise from higher loading of the active phase (CeZrO₂ or Ni-CeZrO₂) in those samples.

Figure 5. The Ce, Zr and Ni mapping for NiCZ/CNT (a) and selected area electron diffraction for Ni and CeZrO₂ nanocrystals supported over CNTs (b).

Figure 6. The N₂ adsorption/desorption isotherms for CZ/CNT, NiCZ/CNT and Ni/CNT catalysts.

Table 1. Textural properties of CZ/CNT, NiCZ/CNT and Ni/CNT catalysts (S_{BET} —BET surface area, V_t —total pore volume, V_{micro} —volume of micropores, V_{macro} —volume of macropores, d —mean pore size).

Sample	S_{BET} (m ² /g)	V_t (cm ³ /g)	V_{micro} (cm ³ /g)	V_{mezo} (cm ³ /g)	V_{macro} (cm ³ /g)	D (nm)
Ni/CNT	585	2.55	0.04	2.18	0.33	17.48
CeZrO ₂ /CNT	255	1.00	0.02	0.97	0.01	15.70
NiCeZrO ₂ /CNT	235	1.12	0.02	1.1	0.00	19.09

2.2. Catalytic Tests of DRM

The performance of obtained catalysts in the DRM reaction was tested in the temperature-programmed (TP) conditions to determine the temperature range for the reaction (Figure 7), and in isothermal mode (Figure 8).

Figure 7. The evolution of CH₄, CO₂, H₂ and CO during tests of dry reforming of methane (DRM) carried out in temperature-programmed (TP) conditions over CZ/CNT (a), NiCZ/CNT (b) and Ni/CNT (c) and corresponding mechanisms of DRM reaction.

Figure 8. CH₄ (a) and CO₂ (b) conversion during DRM on CZ/CNT, NiCZ/CNT and Ni/CNT catalysts.

From the TP tests (Figure 7) it is observed that Ni presence in the sample significantly decreases the temperature of DRM occurrence. The CO + H₂ formation starts at 750 °C for CZ/CNT, 630 °C for NiCZ/CNT and 400 °C for Ni/CNT. Besides, all catalysts differ from each other regarding the reaction mechanism (shown on the right side of each TP test). For the CeZrO₂-containing samples, i.e., CZ/CNT and NiCZ/CNT, some decrease in CO₂ concentration due to its adsorption on the reduced and basic ceria surface is observed at temperatures below the temperature of DRM occurrence. The CO₂ adsorption on CeZrO₂ is followed with its decomposition to CO and ceria-zirconia re-oxidation. In the case of CZ/CNT, methane undergoes partial oxidation to CO and H₂ using the lattice oxygen

from CeZrO₂. That elementary reaction leads to the formation of oxygen vacancies (□) that are next filled with oxygen from CO₂ decomposition. In the case of NiCZ/CNT catalyst, methane adsorbs on the reduced Ni sites and undergoes dehydrogenation. Produced in that way carbon species are oxidized with oxygen from CO₂ decomposition taking place over Ni⁰ or the oxygen vacancies in CeZrO₂. While in the case of Ni/CNT catalyst, both the CH₄ and CO₂ activation occurs over reduced Ni active sites. Dehydrogenation of CH₄ over Ni sites is followed by the oxidation of carbon species with CO₂. It is known that if the rate of methane dehydrogenation is higher than the rate of carbon suppression with CO₂, the Ni sites either will be covered with coke or will act as active sites for the formation of structural carbon species (e.g., CNTs, carbon nanofibers, etc.), whereas the type of carbon deposit formed over the Ni is temperature-dependent.

The CH₄ and CO₂ conversions during DRM after 2 h on-stream at each temperature over CZ/CNT, NiCZ/CNT and Ni/CNT are presented in Figure 8. The performance of Ni/CNT is significantly better than that of CZ/CNT and NiCZ/CNT catalysts. It shows 28 and 10% conversion of CH₄ and CO₂, respectively at a temperature as low as 450 °C, while the CZ/CNT and NiCZ/CNT catalysts are active in DRM above 600 °C. However, some minor activity can be observed in the 500–600 °C range for the latter. According to TEM observations, Ni and CeZrO₂ remained in good contact; thus, one would expect such a catalyst to show at least similar activity to the Ni/CNT. The significantly lower performance of NiCZ/CNT compared to Ni/CNT may arise from the partial coverage of Ni crystals with CeZrO₂; hence, not sufficient exposure of the Ni active sites for CH₄ dehydrogenation. The most frequently used model for DRM is the Langmuir-Hinshelwood one, in which both the CH₄ and CO₂ are adsorbed on the surface. The most widely applied rate-determining step is CH₄ decomposition and the surface reaction of two adsorbed species [49]. Reduced concentration of Ni sites accessible for CH₄ adsorption in NiCZ/CNT compared to Ni/CNT will affect the DRM reaction. The Ni/CNT characterizes with very high SSA (about 2.3 times higher than for NiCZ/CNT) and the access of reagents to well-dispersed Ni nanocrystals is uninterrupted, making it very active in DRM.

At each temperature, the CO₂ conversion was found to be higher than that arising from the stoichiometry of DRM reaction. It can be explained by CO₂ consumption in the reverse water gas shift (RWGS) reaction (Equation (4)), that is known to occur during DRM [50], and in CO₂ deoxidation on the reduced-state active sites (*) (Equation (5)) that can be either oxygen vacancies in the CeZrO₂ lattice or Ni⁰. It must be noted here, that CO₂ deoxidation is an elementary reaction both in the DRM and in the RWGS reactions; however, it can also take place beyond the DRM and RWGS catalytic cycles. From Table 2 it can be seen that the “non-DRM” conversion of CO₂ (i.e., coming from RWGS or CO₂ deoxidation) is the highest for the NiCZ/CNT sample which contains both types of active sites for CO₂ deoxidation. Moreover, it is known that the presence of Zr in ceria lattice increases the rate of formation of oxygen vacancies. It results in higher oxygen capacity, and in consequence—in more important CO₂ deoxidation. The contribution of CO₂ in DRM, RWGS and deoxidation reactions varies depending on the active site supported on CNTs (Figure 9). The “non-DRM” consumption of CO₂ over CZ/CNT is limited to CO₂ deoxidation, whereas over Ni/CNT it is associated to RWGS only. The combination of Ce³⁺ (and oxygen vacancies) with Ni⁰ sites in NiCZ/CNT catalyst results in increased CO₂ consumption owing to the occurrence of RWGS and CO₂ deoxidation, whereas the contribution of the latter is bigger, especially at lower temperatures because of the thermodynamic of RWGS reaction that favours higher temperatures.

The occurrence of RWGS during DRM usually manifests by the H₂/CO < 1, and such a phenomenon is observed in Figure 10. In addition, the decrease of H₂/CO ratio can be caused by the CO₂ deoxidation, that produces CO, thus decreases the overall contribution of H₂ in the product gas. The reverse situation, i.e., the increase of H₂/CO > 1, would speak either for the CH₄ decomposition (Equation (3)) that generates more H₂, or the Boudouard reaction (Equation (2)) that consumes CO. Both reactions can occur during DRM and result in carbon deposition. However, in the presented cases the H₂/CO < 1.

The spent CZ/CNT_s, NiCZ/CNT_s and Ni/CNT_s catalysts were subjected to XRD and TEM analyses. Some minor differences in catalysts composition and their morphology before and after catalytic tests, determined by XRD (Figure 11 and Table 3) and TEM (Figure 12), were noticed to occur. For example, it was calculated from Scherrer equation, that the mean size of CeZrO₂ in [220] direction in CZ/CNT catalyst decreased after catalytic tests (Table 3) but TEM (Figure 12a) shows the presence of bigger CeZrO₂ agglomerates of up to 17 nm dimension. In the case of NiCZ/CNT_s and Ni/CNT_s the increase of Ni and CeZrO₂ crystallites size was noticed, compared to fresh catalysts. Nevertheless, the active phases deposited on CNTs maintained the nanosized character after exposition to DRM mixture at elevated temperatures. Moreover, the XRD of spent Ni/CNT_s proved that NiO that was initially observed in fresh Ni/CNT sample was totally reduced to Ni during DRM reaction, whereas in the case of NiCZ/CNT_s some oxidation of Ni to NiO can be observed. This supports the hypothesis that during DRM, the excess CO₂ can dissociate on reduced active sites, especially on Ce³⁺ and oxidizes them to Ce⁴⁺ (hence, filling the oxygen vacancies in CeZrO₂ lattice). In addition, high oxygen mobility in CeZrO₂ lattice and strong Ni-CeZrO₂ interaction allow the oxidation of Ni⁰ to NiO.

Table 2. The “non-DRM” conversion of CO₂ over CZ/CNT, NiCZ/CNT and Ni/CNT catalysts.

T (°C)	Non-DRM CO ₂ Conversion (%)		
	CZ/CNT	NiCZ/CNT	Ni/CNT
450	-	-	1.0
500	-	20.1	4.0
550	-	30.0	6.3
600	-	27.7	9.7
650	9.4	26.6	8.6
700	16.8	31.8	10.6
750	11.2	26.6	12.5
800	9.0	30.1	14.2
850	11.7	27.3	14.5
900	8.0	26.0	14.5

Figure 9. Contribution of CO₂ in DRM, reverse water gas shift reaction (RWGS) and CO₂ deoxidation reactions during DRM over CZ/CNT (a), NiCZ/CNT (b) and Ni/CNT (c).

Figure 10. The H_2/CO ratio during DRM over CZ/CNT, NiCZ/CNT and Ni/CNT catalysts.

Figure 11. XRD patterns of spent catalysts: CZ/CNT_s, NiCZ/CNT_s and Ni/CNT_s.

Table 3. The mean crystallite size (D) for Ni[111] and CeZrO₂[220] in fresh and spent catalysts.

Fresh Sample	D (nm)		Spent Sample	D (nm)	
	Ni (111)	CeZrO ₂ (220)		Ni (111)	CeZrO ₂ (220)
CZ/CNT	-	9.94	CZ/CNT _s	-	5.03
NiCZ/CNT	6.90	9.88	NiCZ/CNT _s	9.13	10.40
Ni/CNT	14.13	-	Ni/CNT _s	16.76	-

Figure 12. TEM pictures of spent catalysts: CZ/CNT_s (a), NiCZ/CNT_s (b) and Ni/CNT_s (c).

3. Materials and Methods

3.1. Synthesis of the CNT-Supported Metal Catalysts

Three catalysts were synthesized using multiwall carbon nanotubes (Sigma Aldrich, the outer diameter of 6–13 nm; inner diameter of 2–6 nm; length of 2.5–20 μm , purity > 99%) as support. Prior to catalysts syntheses, the CNTs were oxidized (functionalized) in concentrated HNO_3 at 110 $^\circ\text{C}$ for 24 h. After functionalisation the CNTs were washed with distilled water until pH = 7 and dried at 120 $^\circ\text{C}$ /24 h.

All the syntheses of the CNT-supported catalysts were carried out according to the same sequence of steps. In each synthesis, the suspension of 0.1 g of oxidized CNTs in 40 mL of ethanol and 50 mL of distilled was used. The CNT suspension was placed in the three-necked round-bottomed flask connected with the condenser. In order to provide the inert atmosphere during synthesis, the Ar (10 mL/min) flew through the suspension. Each of the metal salts— $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{N}_2\text{O}_7\text{Zr} \cdot x\text{H}_2\text{O}$ (both purchased in Sigma Aldrich)—was dissolved in 10 mL water + acetone mixture (*v/v* 1:1) and instilled (as required; Table 4) into the CNT suspension. The mixture was then sonicated for 1 h. Afterwards, the aqueous solution of NaOH (1M) was instilled into the mixture until pH = 10. The mixture was stirred at room temperature overnight, and then, at 70 $^\circ\text{C}$ for 4 h. After cooling down to the room temperature, the mixture was filtered off under reduced pressure and washed with large amounts of distilled water until the pH was neutral. The obtained material was dried at 120 $^\circ\text{C}$ for 24 h and calcined at 500 $^\circ\text{C}$ for 2 h under flowing argon (20 mL/min). In order to protect the CNT support from being oxidized with NO_x produced during thermal decomposition of nitrates, the calcination was carried out in few steps: 1— heating to 150 $^\circ\text{C}$ (5 $^\circ\text{C}/\text{min}$) followed by 30 min isotherm, 2—heating up to 350 $^\circ\text{C}$ (5 $^\circ\text{C}/\text{min}$) followed by 1 h isotherm, and finally, 3—heating to 500 $^\circ\text{C}$ (2 $^\circ\text{C}/\text{min}$). After the 2 h isotherm at 500 $^\circ\text{C}$, the sample was cooled down to room temperature in flowing Ar. As a result, three catalysts were obtained: Ni/CNT, CeZrO₂/CNT (denoted CZ/CNT) and Ni-CeZrO₂/CNT (denoted NiCZ/CNT). The cerium and zirconium salts were used in amounts allowing the formation of a cerium-zirconium mixed oxide of the following composition: Ce_{0.68}Zr_{0.32}O₂. The composition of prepared catalysts is given in Table 4.

Table 4. The composition of prepared catalysts.

Catalyst	At%			
	C	Ni	Ce	Zr
Ni/CNT	97.8	2.2	-	-
CZ/CNT	97.2	-	1.9	0.9
NiCZ/CNT	94.6	2.5	1.9	0.9

3.2. Catalyst Characterization

The catalysts were characterized using typical analytical methods. The X-ray diffraction (XRD) was performed for 2θ from 10 to 80 $^\circ$ with 0.03 $^\circ$ steps using the MiniFlex diffractometer (Rigaku, Japan, Tokyo) with copper anticathode ($\lambda = 1.54 \text{ \AA}$). The specific surface area (SSA) of the catalyst samples was determined by the N_2 adsorption/desorption at 77 K using the Autosorb 3.01 (Quantachrome Instruments, Boynton Beach, FL, USA). For determining the surface area of catalyst samples, the Brunauer-Emmett-Teller (BET) method was used. The pore volume was calculated using the Barrett-Joyner-Halenda (BJH) method. Before the analyses, the samples were degassed at 150 $^\circ\text{C}$ for 12 h. The morphology of the obtained catalysts was determined by the transmission electron microscopy using the S/TEM Titan 80–300 microscope (FEI Company, Hillsboro, Oregon, UK) equipped with EDAX EDS (energy dispersive X-ray spectroscopy) detector operating at accelerating voltage of 300 kV.

3.3. Catalytic Tests

The performance of CNT-supported catalysts in DRM reaction was determined by tests carried out in the temperature-programmed (TP) and isothermal conditions. All experiments were performed in a U-shape fixed bed reactor placed in an oven equipped with the temperature regulator. Tests were conducted in the atmospheric pressure using the reaction mixture composed of 4 vol.% CH₄, 10 vol.% CO₂ and balanced with Ar. The gas hourly space velocity (GHSV) was 15,000 h^{−1} for each test. The tests in TP conditions were carried out at temperature increasing linearly from 25 to 900 °C with a heating rate of 5 °C/min. The tests in isothermal conditions were conducted at temperatures ranging from 500 to 900 °C; however, the initial temperature was 900 °C and it was decreased by 50° after 2 h on-steam. The same sample was used for each temperature.

4. Conclusions

Three CNT-supported catalysts with well dispersed, nanosized CeZrO₂, Ni-CeZrO₂ and Ni active phases were obtained and tested in DRM reaction carried out in the excess of CO₂ (CO₂/CH₄ = 2.5).

The DRM over obtained catalysts occurred via different mechanisms; however, the common elementary reaction was CO₂ deoxidation that provided oxygen to the catalyst. The presence of oxygen vacancies in partially reduced and basic ceria (in CeZrO₂/CNT and Ni-CeZrO₂/CNT samples) facilitated CO₂ deoxidation, protecting the catalyst from carbon deposition. Oxygen provided to the catalyst via CO₂ deoxidation was used in the reaction of partial oxidation of CH₄ adsorbed on CeZrO₂ or oxidation of carbon species produced on Ni sites as a result of CH₄ dehydrogenation.

The best performance in DRM showed the Ni/CNT catalyst, while the CeZrO₂-containing samples exhibited much lower activity. A significant difference in the performance of Ni/CNT and Ni-CeZrO₂/CNT might have been caused by the partial coverage of Ni nanocrystals with CeZrO₂ in the latter; thus, the reduction in the concentration of Ni sites exposed to reagents. Catalytic tests revealed that the conversion of CO₂ was higher than arising from the stoichiometry of DRM reaction, which was due to the occurrence of RWGS reaction over Ni-containing catalysts and CO₂ deoxidation on CeZrO₂-containing catalysts. The combination of two types of active sites in Ni-CeZrO₂/CNT, i.e., oxygen vacancies and Ni⁰, resulted in increased CO₂ consumption since both the RWGS and CO₂ deoxidation took place.

CNTs as a support material allow to develop significantly the surface area of deposited active phases. The main drawback of DRM process is catalyst deactivation caused by carbon deposition, which is a result of insufficient suppression of carbon species formed during methane dehydrogenation. Since Ce³⁺ is an active site for CO₂ activation followed by the oxidation of carbon species covering the surface of the catalyst during the DRM reaction, the combination of CeZrO₂ and Ni phases over CNT support is a promising solution for developing an active catalyst resistant to carbon deposition. That could be achieved by modifying the synthesis method of Ni-CeZrO₂/CNT, e.g., by the sequential deposition of both active phases.

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