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Effect of Ag-Addition on the Catalytic and Physicochemical Properties of Ni/ZrO₂ Catalyst in Oxy-Steam Reforming of CH₄ and LNG Processes

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Abstract: This work presents, for the first time, the catalytic studies of bimetallic Ag-Ni catalysts in the oxy-steam reforming (OSR) of liquefied natural gas (LNG) to hydrogen generation. The physicochemical properties of monometallic Ni and bimetallic catalysts were investigated using various techniques, such as: BET, TPR-H₂, TPD-NH₃, XRD, TG and SEM-EDS. The catalytic studies showed that the promotion of 20% Ni/ZrO₂ catalyst by silver (by 1 or 2 wt.%) improves the efficiency of the produced hydrogen in the oxy-steam reforming of LNG at high temperature. The promotional effect of silver on the reducibility of a Ni/ZrO₂ catalyst has been proven. The interactions between Ag and Ni have been proven, and explain the catalytic activity of the catalysts in the investigated processes. TG-DTA-MS results obtained for the spent catalysts proved that the small addition of silver to monometallic nickel catalyst reduces the amount of the carbon deposit formed on the catalyst surface during the oxy-steam reforming of LNG process. Obtained results in this work confirmed that liquid natural gas processing may become an alternative to fossil fuels and confirmed the validity of the hydrogen production via oxy-steam reforming of LNG.

Keywords: hydrogen production; oxy-steam reforming of methane; ZrO₂ support; bimetallic Ag-Ni catalysts; silver promotion; nickel catalyst

1. Introduction

Liquefied natural gas (LNG) is a colourless, non-toxic, non-corrosive and clear liquid mixture, containing mainly methane (88.4 to 99.7%) and other light hydrocarbons such as: ethane, propane, butane and nitrogen. LNG is natural gas cooled to the temperature of −162 °C. Its low temperature results in shrinks of the gas volume about 600 times, making its more economical to transport and storage. Overseas and long-distance transport of natural gas via pipeline is not economically feasible. Besides, natural gas has a very low density and is highly explosive; this causes it to be very costly to transport and storage. Therefore, liquefied natural gas is now a cost-competitive and clean fuel, especially for shipping and road transport. LNG can also be turned back into a gas during regasification process. Figure 1 present the global LNG business, which is described as a “value chain” containing elements such as: exploration, liquefaction, shipping and storage/regasification. Nowadays, steam reforming (SR) of natural gas and other hydrocarbons is the main commercial process used to syngas production [1]. This reaction is characterized by the high H₂/CO molar ratio and low selectivity and yield to CO production. However, the SR process is a highly endothermic reaction that makes it

energetically expensive [2,3]. The exothermic partial oxidation of methane (POM) reaction is more promising from the application point of view. The advantages of POM process are the high conversion of raw material and selectivity and short residence time assigned to a H_2 to CO molar ratio ≈ 2 [4,5]. However, POM reaction present also several disadvantages, such as: risk of explosion and catalyst deactivation caused by overheating [6,7].

Figure 1. LNG usage scheme.

An alternative for steam reforming and partial oxidation processes is their combination, namely the oxy-steam reforming (OSR) reaction, which is energetically favourable, because it can run in the autothermal way without the need to supply any external heat [8–11]. The following reactions occur during oxy-steam (OSR) reforming of methane:

The steam reforming of methane (SRM):

The partial oxidation of methane (POM):

The complete combustion of methane (CCM):

The water gas shift reaction (WGS):

The Boudouard reaction:

The methane cracking reaction:

An oxygen introduction into the steam reforming of methane (SRM) facilitates complete methane conversion [12–14]. In addition, in the oxy-steam reforming of methane (OSRM) reaction, the efficiency of CO formation is lower, because it can undergo oxidation process, whereas, the value of hydrogen yield formation is in the range of the value which can be observed for steam reforming of methane

(SRM) and partial oxidation of methane (POM) reactions [6,8]. The coke formation which is popular for POM reactions is reduced when the steam is added. Moreover, the steam addition also improves the efficiency of hydrogen formation [8,15]. Therefore, the OSRM process is the best alternative to POM reaction, because it reduces the carbon deposit formation. On the other hand, OSRM has also an advantage over SRM because increase dynamics and yield of the process [3,16]. The transition metals such as: Rh, Ru and Pt supported on various oxides are commonly used as the catalysts in the SR of methane process. In industry, nickel catalysts are widely used in SRM process to hydrogen production [17]. However, nickel containing catalysts are also active in the decomposition of methane reaction, which leads to carbon and hydrogen formation, result in carbon deposit formation [18,19]. Furthermore, it is well known that the promotion of Ni catalysts by noble metals improves their resistance to coke formation [20–22]. However, precious metals are much more expensive compared to transition metals. Hosseini et al. [23] investigated nickel catalysts supported on Al_2O_3 prepared by traditional (UM-Ni/ Al_2O_3) and under-microwave irradiation (M-Ni/ Al_2O_3) impregnation methods. They determined the effect of preparation method of the catalyst on the catalytic reactivity in the oxy-steam reforming of methane reaction. The activity tests showed that the M-Ni/ Al_2O_3 catalyst exhibited higher methane conversion and about twice time higher value of syngas production compared to UM-Ni/ Al_2O_3 catalyst. They reported that the high catalytic performance of M-Ni/ Al_2O_3 system is related with the small sized (<6 nm) and steadily distributed nickel species which strongly interacted with the Al_2O_3 support. Kaori Yosida et al. [24] studied Ni/ $\alpha\text{-Al}_2\text{O}_3$ catalysts modified by noble metals such as: Pd, Pt, Au, Ir, Rh and Ru prepared by co-impregnation method. The catalytic activity tests were carried out in the oxy-steam reforming of methane process. Authors have found that palladium is the most effective modifier of nickel catalyst among studied noble metals. Moreover, the monometallic Pd catalyst supported on Al_2O_3 is not suitable for the OSRM reaction. Parizotto et al. [25] also investigated the nickel catalysts supported on alumina promoted by silver for steam reforming of methane. The purpose of their work was to determine the effect of the silver addition on the physicochemical, catalytic and coke formation properties of Ni catalysts in the SRM process. They reported that silver addition strongly modified the catalyst surface properties. The CO adsorption spectra recorded during FTIR measurements for Ag-Ni catalysts demonstrate, that the Ag promotion changes the structure of the catalyst surface which is associated with the change of the distributed of the CO-adsorbed species. The stability tests carried out in the SRM process over the bimetallic catalysts containing Ag >0.3 wt.% confirmed their high resistance to carbon deposit formation. Hyun-Seog Roh et al. [26] compared novel Ni/Ce-ZrO₂ with commonly used Ni/MgAl₂O₄ or Ni/MgO catalyst systems in SRM and OSRM processes. The Ni/Ce-ZrO₂ catalyst exhibited high activity and stability in the studied reactions, due to the synergistic effect between cerium and Ni species, resulting from the strong interaction between Ni and Ce-ZrO₂. In addition, their high activity is also explained by the high ability to produce and storage mobile oxygen species during the reaction. Wen-Sheng Dong et al. [27] studied the effect of nickel content on the catalytic properties of Ni/Ce-ZrO₂ catalyst in the partial oxidation, steam and oxy-steam reforming of methane reactions. The 15% Ni/Ce-ZrO₂ catalyst system exhibited the highest activity and stability in all studied processes. The authors explain this result as a balance between two types of active sites, one type of centres associated with an activation of methane and the other for steam or oxygen activation centres. Hongmin Wang et al. [28] characterized and tested the monometallic Ni/HT (hydrotalcite) and bimetallic Ag-Ni/HT catalysts in steam reforming of methane reaction. The kinetic study and DFT calculation were carried out, in order to better understand the effect of Ag addition on the physicochemical and catalytic properties of the studied catalysts. Authors reported that silver substitute the Ni active sites in the crystal. Addition of silver on the surface of the nickel catalyst significantly change the activity of the sites near silver, which destabilizes the adsorption of carbon, hydrogen and intermediates during the reaction. The results also confirmed the sites nearby Ag particles are inactive for the activation of the C–H bond in the CH₄ molecule. In addition, silver is blocking the more active centres of the catalyst, such as edges, steps and Ni(100) centres.

The main goal of the presented paper was to determine the effect of silver addition on the catalytic behaviour of the monometallic Ni catalysts in the oxy-steam reforming of methane and liquified natural gas (LNG) processes. In order to achieve the intended purpose of this work we prepared nickel catalyst supported on ZrO_2 , with 20 wt. % of Ni. Afterwards, the bimetallic Ag-Ni catalysts were prepared by subsequent impregnation method. The physicochemical properties of the investigated catalysts were determined using BET, XRD, SEM-EDS, TPR- H_2 , TPD- NH_3 and TG techniques. In addition, the reactivity results in the oxy-steam reforming of methane and LNG of the investigated systems were correlated with their physicochemical properties.

2. Results and Discussion

2.1. The Syngas Production via OSR of Methane and LNG Reactions

In the first stage of the research, the composition of the investigated catalysts was optimized. The catalytic activity tests in the oxy-steam reforming of methane and liquefied natural gas (LNG) processes were carried out over investigated mono- and bimetallic catalysts. The catalytic activity was expressed as methane/LNG conversion, selectivity to CO and CO_2 , and hydrogen yield for all investigated catalyst systems were determined, in order to correlate them with the physicochemical properties of the investigated catalysts (see Tables 1–3 and Figures 2–6). The oxy-steam reforming of the methane reaction was carried out in the temperature range 700–900 °C. The activity measurements performed in OSR of methane process showed that the increase of the reaction temperature resulted in the increasing of the methane conversion values for monometallic 20% Ni/ ZrO_2 and bimetallic x Ag-20% Ni/ ZrO_2 systems, where x = 1 and 2%, respectively. Only 0.5% Ag-20% Ni/ ZrO_2 catalyst exhibited lower methane conversion at higher reaction temperature (900 °C), compared to the other investigated catalytic systems. The increase of the reaction temperature result in decrease of the hydrogen yield values for all investigated catalysts. The obtained reactivity results clearly showed that the addition of silver to monometallic 20% Ni/ ZrO_2 catalyst result in decrease of the methane conversion values. In the case of 0.5% Ag-20% Ni/ ZrO_2 catalyst, the catalytic measurements confirmed lower methane conversion and H_2 yield compare to the monometallic catalyst. 1% Ag-20% Ni/ ZrO_2 catalyst exhibited the same value of methane conversion, but lower hydrogen yield compared to monometallic Ni catalyst. Only in the case of 2% Ag-20% Ni/ ZrO_2 system the improvement of the hydrogen yield formation in the tested OSR of methane reaction at 700 °C compared to Ni catalyst was detected. This catalyst showed lower methane conversion equal 79 and 81% at 700 °C and 900 °C, respectively. Meanwhile, it exhibited the highest yield of hydrogen generation at 700 °C. This result indicates the promotion effect of silver on catalytic selectivity of the 20%Ni catalyst system towards hydrogen production in OSR of methane reaction at 700 °C (see Figure 2). However, at 900 °C, bimetallic 2% Ag-20% Ni/ ZrO_2 catalyst exhibited lower hydrogen yield and higher selectivity to CO formation compared to the rest of the studied systems. It is also worth emphasizing that monometallic 20% Ni/ ZrO_2 catalyst exhibited high methane conversion in the oxy-steam reforming of methane reaction equal to 97 and 100%, at 700 and 900 °C, respectively. Similar methane conversion values showed bimetallic 1% Ag-20% Ni catalyst. In addition, 20%Ni catalyst showed also the highest hydrogen yield 88% at 900 °C, in the studied OSR of methane process (see Table 1).

In the next stage of the catalytic activity measurements, the oxy-steam reforming of LNG reaction was studied, and the results are given in Tables 2 and 3 and in Figures 3–6, respectively. The OSR of LNG process was performed in the temperature range 400–900 °C. The LNG conversion results are presented as conversion of LNG components, such as: methane, ethane, propane and butane. The results of the activity tests showed that the increase of the reaction temperature result in increase of the LNG components conversion values for all the studied catalytic systems. At 500 °C, only monometallic catalysts exhibited total conversion of ethane, propane and butane. Meanwhile, all bimetallic catalysts exhibited only complete conversion of butane. The catalytic results obtained for all catalytic materials for the reactions carried out at 600 °C indicate that only in the case of

monometallic Ni and bimetallic 0.5%-20% Ni and 1%-20% Ni catalysts total conversion of ethane propane and butane has been confirmed. In the case of 2% Ag-20% Ni catalyst, the activity results obtained at 600 °C confirmed incomplete conversion of methane (7%) ethane (57%) and propane (80%). Starting from a reaction temperature of 600 °C, total conversions of ethane, propane and butane were confirmed for monometallic and bimetallic catalysts, with 0.5 and 1% of silver. Only in the case of the bimetallic catalyst containing 2wt.% of Ag, was incomplete conversion of methane, ethane and propane observed at 700 °C. Moreover, at 900 °C, during the investigated process, incomplete values of methane and ethane conversion were also detected. The activity results indicate that hydrogen yield was the highest for this bimetallic catalysts at 700 and 900 °C. Meanwhile, at low temperature (500 and 600 °C) range, the highest hydrogen yield exhibited 20% Ni/ZrO₂ catalyst. All investigated catalyst systems exhibited an increase of the CO selectivity values with increasing of the reaction temperature. It is also worth emphasizing that for bimetallic catalysts containing 2 wt.% of Ag, the CO was formed only at 900 °C. The opposite trend was observed towards CO₂ formation. The selectivity toward CO₂ formation decreases for monometallic catalyst system above 400 °C and for bimetallic 0.5% Ag-20% Ni/ZrO₂ and 1% Ag-20% Ni/ZrO₂ catalysts above 500 °C. Monometallic 20% Ni/ZrO₂ catalyst system showed the hydrogen formation already at 500 °C in contrast to bimetallic catalysts, for which the hydrogen formation was observed starts from 600 °C for 0.5%-20% Ni and 1% Ag-20% Ni catalysts. Whereas, for 2% Ag-20% Ni/ZrO₂ catalyst, only CO₂ and H₂ products formation up to 700 °C were observed. The highest hydrogen yield value exhibited bimetallic 2% Ag-20% Ni/ZrO₂ catalyst at 700 °C, however, at a low conversion values of LNG components. The comparison of the oxy-steam reforming of methane (OSR of methane) and liquefied natural gas (OSR-LNG) processes showed that in the case of OSR-LNG reaction we observed for all investigated catalysts lower hydrogen production yield, compared to the OSR of methane process.

Table 1. Methane conversion, hydrogen yield and selectivity values towards CO and CO₂ formation in the oxy-steam reforming of methane process over calcined mono- and bimetallic catalysts.

Catalysts	Temp. [°C]	Methane Conversion [%]	CO ₂ Selectivity [%]	CO Selectivity [%]	H ₂ Yield [%]
20% Ni/ZrO ₂	700	97	11	89	91
	900	100	15	85	88
0.5% Ag-20% Ni/ZrO ₂	700	98	14	86	71
	900	82	5	95	62
1% Ag-20% Ni/ZrO ₂	700	96	11	89	83
	900	100	6	94	78
2% Ag-20% Ni/ZrO ₂	700	79	29	71	98
	900	81	3	97	37

Figure 2. The activity results of the investigated Ni and Ag-Ni catalysts in oxy-steam reforming (OSR) of methane process.

Table 2. Conversion values of the hydrocarbons obtained in the oxy-steam reforming of liquefied natural gas (LNG) process over mono- and bimetallic supported catalysts.

Catalysts	Temp [°C]	Methane Conversion [%]	Ethane Conversion [%]	Propane Conversion [%]	Butane Conversion [%]
20% Ni/ZrO ₂	400	19	25	37	100
	500	46	100	100	100
	600	77	100	100	100
	700	98	100	100	100
	900	100	100	100	100
0.5% Ag-20% Ni/ZrO ₂	400	2	14	26	100
	500	6	34	83	100
	600	57	100	100	100
	700	73	100	100	100
	900	81	100	100	100
1% Ag-20% Ni/ZrO ₂	400	0	10	25	100
	500	2	46	86	100
	600	62	100	100	100
	700	72	100	100	100
	900	75	100	100	100
2% Ag-20% Ni/ZrO ₂	400	0	10	20	100
	500	4	36	71	100
	600	7	57	80	100
	700	12	59	82	100
	900	53	95	100	100

Figure 3. The activity results of the 20% Ni/ZrO₂ catalyst in OSR-LNG process. **Figure 4.** The activity results of the 0.5% Ag-20% Ni/ZrO₂ catalyst in OSR-LNG process.

Table 3. The hydrogen yield and selectivity values to CO and CO₂ obtained in the oxy-steam reforming of LNG process over mono- and bimetallic supported catalysts.

Catalysts	Temp [°C]	CO ₂ Selectivity [%]	CO Selectivity [%]	H ₂ Yield [%]
20% Ni/ZrO ₂	400	100	0	0
	500	72	28	58
	600	32	68	74
	700	14	86	57
	900	0	100	63
0.5% Ag-20% Ni/ZrO ₂	400	100	0	0
	500	100	0	0
	600	56	44	63
	700	35	65	66
	900	24	76	54
1% Ag-20% Ni/ZrO ₂	400	100	0	0
	500	100	0	0
	600	48	52	70
	700	39	61	59
	900	18	82	65
2% Ag-20% Ni/ZrO ₂	400	100	0	0
	500	100	0	0
	600	100	0	0
	700	100	0	75
	900	28	72	63

The catalytic activity results of the oxy-steam reforming of methane and LNG processes showed that, in both reactions, the silver addition decrease the values of methane or LNG component conversions. In the case of OSR of methane reaction, we observed also that the bimetallic 2% Ag-Ni catalysts exhibited higher hydrogen yield compared to monometallic nickel catalyst only at 700 °C. Meanwhile, in OSR of LNG process the 1% Ag-20% Ni catalyst showed higher yield of H₂ formation at 700 and 900 °C. At 700 °C, higher hydrogen yield compared to monometallic catalyst exhibited also catalysts with 0.5 and 2 wt. % of Ag loading. In addition, 2% Ag-20% Ni/ZrO₂ system showed the same value of hydrogen yield at 900 °C compared to Ni catalyst. These results confirmed the promotional effect of silver on the selectivity of the catalyst towards hydrogen formation. It is also worth emphasizing that high selectivity towards CO₂ in the oxy-steam reforming of LNG process especially at low temperature range is connected with the oxidation of the produced carbon monoxide or products formed from the decomposition of the hydrocarbons. In addition, low selectivity towards hydrogen formation or the lack of this compound in the products is also connected with its oxidation to water vapour during the process.

Jeong Gil Seo et al. [29] investigated a mesoporous nickel alumina aerogel catalyst prepared by impregnation, single step sol-gel and subsequent CO₂ supercritical drying methods. The catalytic activity of these systems was studied in steam reforming of LNG process. The reaction was performed under atmospheric pressure at 600 °C. Before each catalytic test, catalyst was reduced in a mixture of H₂ and N₂ at 700 °C for 3 h. The Ni/AE-IP and Ni/AE-SS catalysts exhibited a stable catalytic performance. Additionally, the Ni/AE-SS catalyst showed higher LNG components conversion and H₂ yield than Ni/AE-IP catalyst. The high activity of the Ni/AE-SS catalyst was explained by the uniform distribution of metallic nickel particles on the catalyst surface, thereby improving the resistance to carbon deposition and increasing sintering resistance during the steam reforming of LNG reaction. In addition, authors of the work [30] investigated the reactivity of Ni/Al₂O₃-ZrO₂ catalyst prepared by

impregnation method in the mentioned reaction. The carrier was prepared by the sol-gel method, and it was calcined at various temperatures. The main goal of their investigation was to explain the effect of the calcination temperature of the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ support on the catalytic activity of $\text{Ni}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ catalyst in the steam reforming of LNG reaction. They proved that high activity of $\text{Ni}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ (calc. at 1000°C) catalyst was explained by high steam adsorption capacity by $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (calcined at 1000°C) carrier. Wang et al. [28] studied bimetallic Ag-Ni catalysts in reforming of methane process, and they proved, based on both the kinetic and DFT studies, that the sites near Ag particles are inactive for the activation of the C-H bond in the CH_4 molecule. Meanwhile, silver blocks the active centres of the catalyst, such as edges, steps and $\text{Ni}(100)$ centres, which also explains our activity results.

Figure 5. The activity results of the 1% Ag-20% Ni/ZrO₂ catalyst in OSR-LNG process.

Figure 6. The activity results of the 2% Ag-20% Ni/ZrO₂ catalyst in OSR-LNG process.

2.2. The Characterisation of the Physicochemical Properties of the Investigated Catalysts

2.2.1. The Specific Surface Area of the Support and Catalysts

The specific surface area (SSA) measurements were carried out over investigated catalyst systems, in order to determine their specific surface area, monolayer capacity and average pore radius. The specific surface area results are given in Table 4. The ZrO_2 support had the highest values of BET surface area and monolayer capacity, which equals $110 \text{ m}^2/\text{g}$ and $0.26 \text{ cm}^3/\text{g}$, respectively. Introduction of nickel onto ZrO_2 support surface significantly decrease of the specific surface area value of the monometallic nickel catalyst. However, in the case of 20% Ni/ZrO_2 catalyst and the ZrO_2 support,

we observed that the same value of the average pore radius was equal to 3.4 nm. Moreover, the silver addition into monometallic 20% Ni/ZrO₂ catalyst caused the slight decrease of the BET surface area values for the bimetallic catalysts. In the case of the monolayer capacity value, we did not observed significant changes. The average pore radius values for the bimetallic supported catalysts were slightly higher compare to monometallic nickel catalyst and equal 3.8 nm. Norazimah Harun et al. [31] investigated Ni(15)/Al₂O₃ catalysts promoted by Ag (1, 3 and 5 wt.%), synthesized by impregnation method. They proved that the introduction of silver on the monometallic nickel catalyst surface caused the decrease of the BET surface area and slightly increased the average of the pore diameter (see Table 4).

Table 4. Brunauer-Emmett-Teller (BET) surface area, monolayer capacity and average pore size for supports, mono- and bimetallic supported catalysts.

Catalytic Materials	BET Surface Area [m ² /g]	Monolayer Capacity [cm ³ /g]	Average Pore Radius [nm]
ZrO ₂	110	0.26	3.4
20% Ni/ZrO ₂	77	0.18	3.4
0.5% Ag-20% Ni/ZrO ₂	66	0.17	3.8
1% Ag-20% Ni/ZrO ₂	69	0.18	3.8
2% Ag-20% Ni/ZrO ₂	69	0.19	3.8

2.2.2. The Surface Acidity of the Catalysts Surface

The temperature programmed desorption of ammonia measurements (TPD-NH₃) was done to examine the total acidity and distribution of the acid centres on the catalyst surface of the investigated support, mono- and bimetallic catalytic systems. The acidity measurements are shown in Table 5. The obtained results confirmed the occurrence of three types of acid centres on the catalytic surface, namely: weak, medium and strong acid sites. The lowest total acidity value of 0.10 mmol/g showed only ZrO₂ support. Introduction of the nickel onto the support surface caused the two-fold increase of the total acidity value. Moreover, the silver addition onto the monometallic nickel catalyst caused the same effect. Meanwhile, the results obtained for the bimetallic catalysts x Ag-20% Ni/ZrO₂ showed that the total acidity of the catalytic systems decreases with increasing silver content in the investigated catalysts. One can notice that for all catalytic systems the highest amount of acid centres of medium and weak strength were detected.

Table 5. The amount of NH₃ adsorbed on support surface (calcined in an air atmosphere for 4 h at 400 °C), mono- and bimetallic reduced catalysts (reduction “in situ” at 500 °C in a mixture of 5% H₂-95% Ar mixture), calculated from the TPD-NH₃ profiles.

Catalytic Materials	Total Acidity [mmol/g]	Weak Centres [mmol/g]	Medium Centres [mmol/g]	Strong Centres [mmol/g]
	100–450 °C	100–300 °C	300–450 °C	>450 °C
ZrO ₂	0.10	0.05	0.04	0.01
20% Ni/ZrO ₂	0.22	0.12	0.09	0.01
0.5% Ag-20% Ni/ZrO ₂	0.49	0.23	0.23	0.03
1% Ag-20% Ni/ZrO ₂	0.44	0.23	0.18	0.03
2% Ag-20% Ni/ZrO ₂	0.43	0.23	0.18	0.02

2.2.3. Reduction Behaviour of the Catalytic Materials

The temperature programmed reduction measurements (TPR-H₂) were performed in order to determine the reduction behaviour of the studied catalysts, and to explain the interactions which take

place between the active phase and support components of the investigated mono- and bimetallic nickel catalysts. The TPR- H_2 profiles recorded for the studied catalysts are presented in Figure 7.

Figure 7. TPR profiles of mono- and bimetallic catalysts calcined at 400 °C in an air atmosphere for 4 h.

The temperature programmed reduction profile of ZrO_2 (result not shown in this paper) support showed two reduction peaks located in the temperature range 250–350 °C and 470–520 °C, respectively [32]. According to the literature data [32,33], the first and the second reduction effects are associated with the reversible hydrogen uptake of the ZrO_2 surface. Meanwhile, the authors of the work [34] reported that they did not observe any reduction peaks on the TPR profile recorded for ZrO_2 material. They claimed also that only the ZrO_2 surface near the metal particle is slightly reduced at high temperature. The TPR profile of monometallic 20% Ni/ ZrO_2 catalyst shows three reduction peaks located at about 220, 345 and 430 °C, respectively. The first reduction stage marked in the Figure 7 as peak II is assigned to the reduction of free NiO species (T_{max} 220 °C). The next two unresolved reduction effects located in the temperature range 280–500 °C, with a maximum of the hydrogen consumption positioned at about 345 and 430 °C are associated with the reduction of NiO species differently interacted with the carrier. The second reduction peak is attributed to the reduction of NiO weakly interacting with the carrier. The third reduction peak (marked as peak IV in Figure 7) visible on TPR profile is connected with the reduction of NiO strongly interacted with the support. Ren et al. [35] also studied the reduction behaviour of Ni/ ZrO_2 catalyst and they also observed three reduction peaks at 324, 344 and 385 °C on the TPR profile. They assigned the low and high reduction temperatures peaks to NiO species, weakly and strongly interacting with the support. The reduction peaks positioned at 324 and 344 °C were associated with NiO species that are of similar nature to pure bulk NiO. Meanwhile, the reduction peak located at 385 °C was attributed to NiO species interacting with the support, whereas, the TPR profiles recorded for bimetallic Ag-Ni catalysts show four reduction stages connected with the reduction of silver oxide and NiO species.

The first low temperature reduction effects visible for all bimetallic catalysts in the temperature range 100–190 °C are assigned to the reduction of silver oxide (see Figure 7). The first reduction peak for the 0.5% Ag-20% Ni bimetallic catalyst associated with the reduction of silver oxide is observed for a maximum of hydrogen consumption located at 135 °C. Increasing the silver content to 1 wt.% shifts the observed reduction peak to a temperature of 110 °C. However, the maximum of the same reduction effect in the case of the catalyst with the highest silver content is visible at a temperature of 125 °C (see Figure 7). The second reduction stages visible on the TPR profiles of bimetallic catalysts are associated with the reduction of unbounded NiO. Their low intensity decreases with the increasing of the Ag content in the catalytic material. This reduction stage is visible for monometallic catalyst at 220 °C. On the other hand, for bimetallic catalysts containing 0.5, 1 and 2 wt.% of silver, the same effects are visible at 175, 140 and 130, respectively (see Figure 7). The third reduction peak visible on the TPR profile of 0.5% Ag-20% Ni catalyst, with the maximum at 320 °C attributed to the reduction of NiO weakly interacted with the support. The same reduction steps for the rest of the bimetallic catalysts were visible at 335 and 330 °C, for 1% Ag-20% and 2% Ag 20% Ni catalysts, respectively. The last reduction peaks of the bimetallic catalysts assigned to the reduction of NiO strongly interacted with the support are located at 420, 410 and 410 °C for 0.5% Ag-20% Ni, 1% Ag-20% Ni and 2% Ag-20% Ni catalysts, respectively. In the case of these high-temperature peaks, a shift of their maxima towards a lower reduction temperature compared to the monometallic catalyst was confirmed. The reduction studies clearly show that the increase in silver content in the case of bimetallic catalysts shifts the reduction peaks towards the lower temperature range. In addition, in the case of bimetallic catalysts, the intensity of the observed reduction effects related to the reduction of NiO strongly interacting with the support decreases compared to the same effect observed for the nickel catalyst. These results indicate that silver addition facilitates the reduction of NiO species. Hengne et al. [36] studied the reducibility of the monometallic and bimetallic Ag-Ni/ZrO₂ catalysts and they detected two H₂ consumption peaks in the temperature range 270–520 °C, connected with the sequential reduction of Ni²⁺ to Ni⁰. Furthermore, for the bimetallic Ag-Ni catalyst also two H₂-TPR peaks located at low temperature with two maxima at 265 and 485 °C were detected. These effects were ascribed to the reduction of silver oxide and NiO species. Kaori Yoshida et al. [24] reported that the addition of noble metal on the surface of the Ni based catalyst facilitates its reduction behaviour. This effect is explained by the flows of hydrogen from the silver to NiO surface which improves its reduction explained by the spillover effect. However, in the oxy-steam reforming of methane reaction, the reducibility of partially oxidized species derived from the metal particles is very important. The amount of the reduced species in the OSRM process dependent on the reduction rate of the partially oxidized species and the oxidation rate of the metal species. In addition, in order to evaluate the influence of the silver on the reducibility of the Ni catalysts the reduction degree of the monometallic and bimetallic catalysts were determined, based on the hydrogen consumption peaks and the calculated results are presented in Table 6. Total H₂ consumption calculated for monometallic Ni catalysts was 2.7 mmol/g_{cat}. Meanwhile, the addition of 0.5 wt.% of Ag into monometallic systems practically did not lead to any change in the value of hydrogen consumption. The calculated hydrogen consumption for this bimetallic catalyst was 2.65 mmol/g_{cat}. The calculated results show that increasing of the Ag content in the catalytic material to 1 and 2 wt.% of Ag leads to an increase in the hydrogen consumption from 2.65 mmol/g_{cat} recorded for 0.5% Ag-20% Ni to 3.03 and 2.81 (see Table 7), for the bimetallic catalysts with higher content of Ag. It is also worth emphasizing that, for all catalysts, the incomplete reduction of NiO species was confirmed. The incomplete reduction can be explained by the strong interaction between NiO and the support component [32].

To further confirm the promoting effect of silver on the reduction of nickel catalysts, Table 7 presents the results of the deconvolution of the observed reduction peaks of mono and bimetallic catalysts. Table 7 shows the contribution of each peak to the total area of TPR peaks attributed to the reduction of various forms of nickel oxide and silver oxide. In addition, it presents the maxima of each reduction peak. The results presented in Table 7 clearly show that the addition of silver decreases

the intensity of the peaks attributable to the reduction of NiO strongly interacting with the support (IV-peak), at the same time increasing the intensity of the peaks attributed to NiO weakly interacting with the carrier. On the other hand, the intensity of the reduction peaks attributed to the reduction of free nickel oxide decreased in the case of bimetallic catalysts, compared to the same effect recorded for the nickel catalyst. The presence of reduction peaks at a lower temperature for bimetallic catalysts is evidence that there was an interaction between metallic silver and nickel oxide. The shift of the reduction profiles towards the lower temperature range proves that the addition of silver facilitates the reduction of nickel oxide species. This reduction behaviour has a strong influence on the reactivity results, in both the studied oxy-steam reforming of methane and LNG processes. It is also worth noting that the observed reducing behaviour confirms the interaction between metallic silver and nickel oxide, which may also confirm the alloying process [37].

Table 6. Hydrogen consumed during the temperature programmed reduction run and the estimated reduction degree for the nickel and bimetallic catalysts.

Catalysts	Total H ₂ Consumption [mmol/g _{cat}]	Reduction Degree of NiO
20% Ni/ZrO ₂	2.70	80
0.5% Ag-20% Ni/ZrO ₂	2.65	78
1% Ag-20% Ni/ZrO ₂	3.03	88
2% Ag-20% Ni/ZrO ₂	2.81	82

Table 7. Reduction data for the monometallic Ni and bimetallic Ag-Ni catalysts after calcination in air for 4 h at 400 °C.

Catalysts	Peak Contribution to the Overall TPR Peak Area (%)			
	I-Peak (T _{max})	II-Peak (T _{max})	III-Peak (T _{max})	IV-Peak (T _{max})
20% Ni/ZrO ₂	-	8 (220 °C)	55 (345 °C)	37 (430 °C)
0.5% Ag-20% Ni/ZrO ₂	1.5 (135 °C)	0.5 (175 °C)	90 (320 °C)	8 (420 °C)
1% Ag-20% Ni/ZrO ₂	2 (110 °C)	1 (150 °C)	86 (335 °C)	11 (410 °C)
2% Ag-20% Ni/ZrO ₂	2 (125 °C)	1 (140 °C)	83 (340 °C)	14 (410 °C)

2.2.4. The Crystalline Structure of the Investigated Catalysts

The X-ray diffraction studies (XRD) were used to determine the phase composition of the investigated catalytic materials being after calcination and the reaction processes. The calcination process was performed at 400 °C for 4 h, whereas the oxy-steam reforming of LNG reaction process was carried out using a fixed bed reactor in the temperature range 400–900 °C. Figure 8 presents the diffraction curves recorded for support, mono- and bimetallic catalysts after the calcination process. The XRD pattern recorded for ZrO₂ support showed the diffraction peaks assigned to ZrO₂-Monoclinic (positioned at 2θ angle: 24.6, 28.4, 31.5, 34.5, 35.2, 41.0, 43.4, 45.2, 49.4, 50.3, 54.2, 55.7, 60.2, 62.9, 66.0, 68.8 and 75.6), ZrO₂-Tetragonal (positioned at 2θ angle: 30.5, 34.5, 35.2, 58.3, 60.2 and 62.9) phases. Meanwhile, XRD patterns recorded for the calcined mono- and bimetallic catalysts showed that the peaks assigned to tetragonal and monoclinic structures of ZrO₂ phases also reflex attributed to NiO (positioned at 2θ angle: 37.3, 43.2, 62.8 and 75.5) phase. It is worth mentioning that, for the bimetallic catalysts, the diffraction peaks assigned to the silver oxide phase were not observed on the XRD patterns; this is explained by the detection limit of the XRD technique [9]. The phase composition studies for the spent bimetallic catalysts in the oxy-steam reforming of LNG process were also performed in this work. XRD curves recorded for the spent bimetallic Ag-Ni catalysts showed the diffraction peaks attributed to ZrO₂ (positioned at 2θ angle: 24.6, 28.4, 31.5, 34.5, 35.5, 41.0, 41.6, 45.6, 49.4, 50.1, 51.9, 54.2, 55.7, 57.3, 58.3, 60.2, 61.7, 62.5, 62.9, 65.8, 69.3 and 71.7), NiO (positioned at 2θ angle: 37.3, 43.4, 62.8, 75.5

and 79.1), Ni (positioned at 2θ angle: 44.5, 51.9 and 76.5) and Ag (positioned at 2θ angle: 38.1, 44.5, 64.4 and 77.5) phases (see Figure 9). These results clearly confirmed the partial reduction of bimetallic nickel catalysts after OSR of LNG process. The existence of other phases on the diffraction curves of the bimetallic catalysts were not detected by the XRD technique.

Figure 8. Powder patterns of the support, mono- and bimetallic supported catalysts calcined in an air atmosphere at 400 °C for 4 h.

Figure 9. Powder patterns of the spent bimetallic supported catalysts in the oxy-stream reforming of LNG process.

In addition, the average size of NiO and Ni crystallites were determined for calcined and spent catalysts, respectively. The crystallites size were calculated using the Scherrer's formula [32]. The results of the crystallites size of NiO species for calcined mono- and bimetallic catalysts are given in Table 8. The obtained results show that the largest crystallites size of NiO was detected for the 20% Ni/ZrO₂

and 0.5% Ag-20% Ni/ZrO₂ catalysts. Meanwhile, the increase of the silver content in the investigated samples to 1 and 2 wt.% of Ag result in decrease of the average size of the NiO crystallites to 17 and 18 nm, respectively. Subsequently, the crystallites of metallic nickel for the spent mono- and bimetallic catalysts were also estimated (see Table 9). The obtained results clearly showed that all catalysts exhibited similar size of the Ni crystallites. Bimetallic catalysts with 0.5 and 1 wt.% of silver showed similar average size of metallic nickel, while both monometallic catalysts 20% Ni and bimetallic 2% Ag-20% Ni system had 35 and 36 nm, respectively (see Figure 9).

Table 8. The size of the metallic nickel oxide crystallites estimated by the Scherrer method for a NiO peak (200), for an angle of $2\theta = 43.276^\circ$, obtained from XRD measurements performed for calcined catalysts.

Catalyst	The Size of NiO Crystallites [nm]
20% Ni/ZrO ₂	32
0.5% Ag-20% Ni/ZrO ₂	33
1% Ag-20% Ni/ZrO ₂	17
2% Ag-20% Ni/ZrO ₂	18

Table 9. The size of the metallic nickel crystallites calculated from the XRD measurements of spent Ni catalysts (after catalytic tests performed in the oxy-stream reforming of LNG process).

Catalyst	The Size of Metallic Ni Crystallites [nm]
20% Ni/ZrO ₂	35
0.5% Ag-20% Ni/ZrO ₂	39
1% Ag-20% Ni/ZrO ₂	39
2% Ag-20% Ni/ZrO ₂	36

In the next part of the phase composition studies, in order to determine the interaction between the active phase component during the reduction process the XRD “in situ” measurements were done for the selected bimetallic catalyst (2% Ag-20% Ni). The phase composition studies performed during the reduction process of the bimetallic 2% Ag-20% Ni/ZrO₂ catalyst performed in hydrogen were given in Figure 10. The diffraction curve of the studied system recorded at 100 °C showed the presence of NiO, as well as crystallographic ZrO₂ phases (tetragonal and monoclinic). The increase of the reduction temperature up to 300 °C result in the appearance on the XRD curve the phases ascribed to metallic nickel, nickel oxide and crystallographic structures of ZrO₂ (tetragonal and monoclinic phases). Further increasing the reduction temperature did not change the phase composition of the investigated catalytic system up to the final temperature. The only change was the slight shift of the reflexes assigned to metallic nickel phase towards the lower 2θ angle values. Ni and Ag crystallize in identical crystallographic systems (regular) and space groups (Fm-3m), which facilitates the formation of solid solutions by these metals. However, the results presented in Figure 10 show that, despite a small amount of Ag (2 wt.%) in the sample after the reduction of the main peak (111), Ag ($2\theta = 37.7$) is clearly visible. So, the observed shift of the reflexes assigned to the metallic Ni is probably associated with the shrinking of the sample at higher temperatures. The XRD results obtained in this study do not clearly confirm the alloying process between metallic nickel and silver. However, based on the XRD measurements, the alloying process of both metals cannot be ruled out.

2.2.5. The Morphology and the Elemental Composition of the Surface of the Investigated Catalysts

The surface morphology of the studied mono- and bimetallic supported catalysts were performed using scanning electron microscopy (SEM). The qualitative elemental analysis of the selected surface, marked by the points or straight line, were carried out by using an energy dispersive detector.

The SEM-EDS measurements were carried out on the surface of the mono- and bimetallic catalysts. The SEM-EDS results are given in Figures 10–12 SEM images and EDS spectra's recorded for the calcined catalysts clearly confirmed the composition of the investigated mono- and bimetallic supported catalysts. Figure 11 presents the SEM images which confirmed the occurrence for 20% Ni/ZrO₂ system; the elements such as: nickel and zirconium. In the case of the bimetallic systems x Ag-20% Ni/ZrO₂, SEM-EDS analysis showed the presence of Zr, Ni and Ag on the surface of the catalysts. In the next part of the morphology studies, the selected areas located on the investigated catalysts were analysed (see Figures 12 and 13). The selected areas were marked by the points or straight line. The point scan allowed one to focus the x-ray beam on a single point and to compare their composition. The surface analysis performed for the 1% Ag-20% Ni/ZrO₂ catalyst is presented in Figure 12. In the case of bimetallic catalysts containing 1 wt.% of Ag five points were selected in different sample surface spots. The spectra collected for 1% Ag-20% Ni catalyst were marked from 1 to 5. The analysis of the first, second and fourth points located close to each other on the sample surface showed the simultaneous occurrence of the Ag, Ni, Zr and O elements. Meanwhile, in the case of 3 and 5 points, the recorded spectra confirmed the occurrence only in Ni, Zr and O elements. Figure 13 presents the results of the surface analysis of the 0.5% Ag-20% Ni/ZrO₂ catalyst. In the case of the surface analysis of this system, the spectra from four points were also collected. In addition, an analysis of the surface marked by a straight line was done. As a result of the analysis, we received a graph showing the concentration of individual elements present on the surface along the tested line. The obtained results clearly indicate the changes in the content of each elements along the investigated line. A surface analysis carried out along the line showed that in the scanned range from 4 to 8 microns, we observed the increase of the silver content and decrease of the nickel content. This result confirm that Ag cover Ni species and can confirm the interaction between nickel with silver. This behaviour agree well with the literature data [28,38] and agree well with our previous reduction studies. The interaction between Ag and Ni explain the reactivity results obtained in the studied processes. Moreover, above 9 microns, the zirconium content increases significantly simultaneously with a decrease in the nickel content. Meanwhile, the spectra's collected from the indicated points located close together confirmed the occurrence of silver, nickel, zirconium and oxygen (points 1 and 4). Whereas, for others investigated points (points 2 and 3) located on the surface, only the presence of nickel, oxygen and zirconium were detected. The obtained results of SEM images, points and line spectra analysis correlate well with each other.

Figure 10. Powder patterns recorded for the 2% Ag-20% Ni catalysts during the reduction process, performed in a hydrogen atmosphere in the temperature range 100–800 °C.

Figure 11. SEM images of mono- and bimetallic nickel catalysts.

Figure 12. SEM images, EDS spectra collected from the marked points for bimetallic 1% Ag-20% Ni/ZrO₂ catalyst.

Figure 13. SEM images, EDS spectra collected from the marked points and line analysis recorded for bimetallic 0.5% Ag-20% Ni/ZrO₂ catalyst.

2.2.6. Thermal Analysis of the Selected Catalytic Materials

The reforming processes are usually performed on nickel-based catalysts. The disadvantage of nickel catalysts is the risk of coke formation on the catalysts surface during the reforming process, which leads to their deactivation. The carbon deposit can be formed during light hydrocarbon decomposition (Equation (1)), or during CO decomposition reaction (Boudouard reaction, Equation (2)) [39,40].

Accordingly, the resistance to the carbon deposit formation on the catalyst surface was investigated in this work using TG-DTA-MS technique. The obtained results showed that independently of the type of the oxy-steam reforming of methane (Figure 14) or LNG (Figure 15) processes the three stages of the carbon deposit oxidation process were observed on MS profiles. The three peaks of the carbon deposit oxidation steps were observed with maxima at 120 °C, 300 °C and 680–690 °C, respectively. MS profiles of CO₂ recorded for bimetallic catalysts are very similar. It is also worth noting that the 2% Ag-20% Ni bimetallic catalyst exhibited the lowest amount of carbon deposit. The first peak visible on the MS spectra can be assigned to an amorphous carbon type. The second visible peak on the MS spectra's is attributed to the oxidation step of the oligomerized carbon species, which is signed as β carbon (Cβ) or carbides. This kind of carbon is a typical type of carbon created during methane reforming processes [41]. The last peak, which is also the widest and the highest, can be related to graphite carbon (Cγ) bulk carbides (γ-carbon).

Figure 14. The MS profiles for $m/z = 44$ (CO_2) of bimetallic Ag-Ni/ ZrO_2 catalysts after oxy-steam reforming of methane reaction.

Figure 15. MS profiles for $m/z = 44$ (CO_2) obtained during the thermal analysis performed in an air atmosphere of the spent catalysts in OSR of LNG process (after 12 h of the reaction).

In the case of monometallic nickel catalysts $20\%\text{Ni}/\text{ZrO}_2$ three peaks of CO_2 desorption during carbon deposition oxidation were also observed at the same temperatures (130, 300 and 690 °C—see Figure 15). The peak of CO_2 formation, with the maximum at 130 °C (see MS profile), is assigned to the removal of amorphous carbon. The second peak is attributed to the oxidation step of the oligomerized carbon species, which is signed as β carbon ($\text{C}\beta$), or carbides. While, the last peak, located at about 690 °C, is connected with the oxidation of graphite carbon ($\text{C}\gamma$) bulk carbides [32]. It is also worth noting that, in the case of this system, we observed the highest intensity of CO_2 desorption peak at high temperature compared to the bimetallic catalysts containing 0.5 and 2 wt.% of Ag (see Figure 15).

This result showed that a small addition of silver reduces the amount of the carbon deposit formation during the oxy-steam reforming of LNG process. Parizotto et al. [25] reported about the high stability of the bimetallic Ag-Ni catalysts in reforming of methane process, which exhibited high resistance to coke deposition. This behaviour was caused by the geometric effect of Ag, changing the structure of Ni centres on which the nucleation and growth of graphitic structure take place and by the decrease of the carbon deposit formation rate. In addition, DFT and kinetics investigations showed that the apparent activation energy increases with increasing of the Ag content on the catalyst surface, which further explains our results of catalytic activity.

3. Experimental

3.1. Supports and Catalysts Preparation

In the preliminary step, the ZrO_2 support was prepared by precipitation method. Aqueous solution of 1 mol/L zirconium nitrate was vigorously stirred at 80 °C, and a concentrated ammonia solution was added by dropwise addition until the pH reached values of between 10 and 11, respectively. Next, the resulting mixture was stirred for 30 min. The precipitate was washed in deionised water and dried for 12 h at 120 °C, and calcined in air atmosphere for 4 h at 400 °C. Monometallic nickel catalyst was prepared by wet impregnation method using prepared ZrO_2 systems as a support. In our previous studies, we confirmed that the optimal nickel content in Ni/ ZrO_2 catalysts was 20 wt.% of Ni. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used as a precursor of metal. Bimetallic x Ag-20% Ni/ ZrO_2 catalysts were prepared by subsequent impregnation method. The Ag precursor was silver nitrate and the metal loading in bimetallic x Ag-20% Ni supported catalysts were x = 0.5, 1 and 2 wt.%, respectively. The supported mono- and bimetallic catalysts were then dried for 2 h at 120 °C, and calcined for 4 h in an air atmosphere at 400 °C.

3.2. Characterization of the Catalytic Material

The catalyst surfaces morphology was studied using S-4700 Scanning Electron Microscopy HITACHI (Tokyo, Japan), equipped with an energy dispersive spectrometer (ThermoNoran, Madison, WI, USA) (SEM-EDS). The Brunauer-Emmet-Teller (BET) specific surface area and porosity of support and catalysts were determined using Sorptomatic 1900 Carlo-Erba apparatus (Surface Area and Porosity Analyzer, Micromeritics Instrument Corporation, Norcross, GA, USA). The crystalline structure of the investigated support and catalysts was obtained using the X-ray diffraction technique (XRD). X-ray diffraction patterns were recorded on a PANalytical X'PertPro MPD diffractometer in Bragg-Brentano reflecting geometry (Malvern Panalytical Ltd., Malvern, United Kingdom). $\text{Cu K}\alpha$ radiation ($\lambda = 154.05$ pm) from a sealed tube was used in the 2θ angle range 5–90°. The temperature programmed reduction (TPR- H_2) measurements were carried out in an automatic TPR system AMI-1 (Altamira Instruments, Pittsburgh, PA, USA), in the temperature range of 25–900 °C with a linear heating rate of 10 °C min^{-1} . The temperature programmed desorption of ammonia (TPD- NH_3) was carried out in the temperature range 100–600 °C using NH_3 as a probe molecule. The mono- and bimetallic supported catalysts before each TPD- NH_3 experiment were reduced at 500 °C, in a mixture of 5% H_2 -95% Ar. The type of carbon deposition was determined by TG-DTA-MS technique. The measurements were carried out in air flow (40 cm^3/min), in the temperature range 20–700 °C, with linear temperature rate increase 10 °C/min using sample weight c.a. 10–20 mg. The investigations were carried out using the SETSYS 16/18 thermal analyzer from Setaram (Caluire, France) and quadrupole mass spectrometer Balzers (Germany).

3.3. Catalytic Activity Measurements in Oxy-Steam Reforming of Methane or LNG

Catalysts activity tests of the investigated catalysts were tested in the oxy-steam reforming of methane and liquefied natural gasses (LNG) reactions using a flow quartz reactor under atmospheric pressure. LNG gas used in catalytic activity tests contain 5% methane, 0.4% ethane, 0.2% propane

and 0.05% butane. The total flow rate was kept at 51 mL/min and the Ar was used as the balance gas. The catalyst load was 0.2 g and the stream composition was: CH₄/LNG:H₂O:O₂ = 1:3:0.4 (molar ratio). The reaction was carried out in temperature range 400–900 °C. The analysis of the organic products formed during the reaction was carried out using on-line gas chromatograph, equipped with a FID detector (120 °C) and HAYE SEP-Q 80/100 column (100 °C). The inorganic products were detected using gas chromatograph equipped with a TCD detector (150 °C, 120 mA), and Silica-Gel-GD12 80/100 column (30 °C). Material balances on carbon were calculated to verify the obtained results. The methane or LNG conversion to gas products was calculated using Equation (3):

$$C_xH_Y \text{ conversion (\%)} = \left(1 - \frac{n_{out} C_xH_Y}{n_{in} C_xH_Y}\right) \times 100\% \quad (3)$$

where:

$n_{in} C_xH_Y$ -the moles of hydrocarbon (CH₄, C₂H₆, C₃H₈ and C₄H₁₀) at the reactor inlet;

$n_{out} C_xH_Y$ -the moles of hydrocarbon (CH₄, C₂H₆, C₃H₈ and C₄H₁₀) at the reactor outlet;

The selectivity toward hydrogen, carbon monoxide and carbon dioxide formation were calculated using Equations (4)–(7):

$$\text{CO selectivity (\%)} = \left(\frac{n_{out} \text{ CO}}{n_{out} \text{ CO} + n_{out} \text{ CO}_2}\right) \times 100\% \quad (4)$$

$$\text{CO}_2 \text{ selectivity (\%)} = \left(\frac{n_{out} \text{ CO}_2}{n_{out} \text{ CO} + n_{out} \text{ CO}_2}\right) \times 100\% \quad (5)$$

$$\text{H}_2 \text{ yield (\%)}_{\text{for OSRM}} = \left(\frac{\frac{n_{out} \text{ H}_2}{2.5}}{\sum(n_{in} C_xH_Y) - \sum(n_{out} C_xH_Y)}\right) \times 100\% \quad (6)$$

$$\text{H}_2 \text{ yield (\%)}_{\text{for OSR-LNG}} = \left(\frac{\frac{n_{out} \text{ H}_2}{2.73}}{\sum(n_{in} C_xH_Y) - \sum(n_{out} C_xH_Y)}\right) \times 100\% \quad (7)$$

where:

$n_{out} \text{ CO}$ -the moles of the CO at the reactor outlet;

$n_{out} \text{ CO}_2$ -the moles of the CO₂ at the reactor outlet;

$n_{out} \text{ H}_2$ -the moles of the H₂ at the reactor outlet;

$\sum(n_{in} C_xH_Y)$ -the sum of the moles of the hydrocarbons (CH₄, C₂H₆, C₃H₈ and C₄H₁₀) at the reactor inlet;

$\sum(n_{out} C_xH_Y)$ -the sum of the moles of the hydrocarbons (CH₄, C₂H₆, C₃H₈ and C₄H₁₀) at the reactor outlet.

4. Conclusions

This work provides evidence that silver addition to nickel catalyst has a significant impact on the activity and selectivity of the Ni catalysts, in both the oxy-steam reforming of methane and LNG processes. The syngas production in the oxy-steam reforming of liquefied natural gas (LNG) process was carried out over investigated mono- and bimetallic supported catalysts. The physicochemical properties of the catalysts were investigated by TPR, BET, XRD, TPD-NH₃, SEM-EDS and TG techniques. The catalytic activity results confirmed the promotional effect of silver on the selectivity of the catalyst towards hydrogen formation. The results obtained in the OSR of LNG process proved that the 1% Ag-20% Ni catalyst showed higher yield of H₂ formation at 700 and 900 °C compared to monometallic Ni catalyst. Meanwhile, at a temperature of 700 °C, the catalysts with 0.5 and 2 wt.% of silver showed a higher yield of hydrogen production compared to the monometallic catalyst. In addition, the 2% Ag-20% Ni/ZrO₂ system showed the same hydrogen formation efficiency at 900 °C as the Ni catalyst. The lower catalytic activity of the bimetallic catalysts in the oxy-steam reforming of methane and

LNG processes can be explained by the interactions between Ag and Ni species. The lower activity of bimetallic catalysts in OSR of methane agree well with the literature data. It has also been found that the addition of silver to the monometallic catalyst increases the total acidity. The catalytic activity measurements showed that catalysts with higher total acidity showed lower catalytic activity in the investigated processes. In order to explain the observed differences in the catalytic activities of the investigated catalysts, it is necessary to conduct more detailed studies on the structure and interactions between the components of the catalysts, as well as between active phase components and support. The TPR-H₂ measurements confirmed that silver addition to the nickel catalysts facilitates their reducibility. TPR measurements showed a shift of the reduction steps recorded for the bimetallic catalysts towards a lower temperature range compared to the monometallic Ni catalyst. This reduction behaviour has a strong influence on the reactivity results in both the studied oxy-steam reforming of methane and LNG processes. Thermal analysis of the spent catalysts proved that the small addition of silver to the monometallic nickel catalyst reduces the amount of the carbon deposit formed on the catalyst surface during the oxy-steam reforming of LNG process.

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