Article

Hydrogen Production on Cu-Ni Catalysts via the Oxy-Steam Reforming of Methanol

Magdalena Mosinska ^{1,*}, Natalia Stępińska ¹, Waldemar Maniukiewicz ¹ , Jacek Rogowski ¹, Agnieszka Mierczynska-Vasilev ² , Krasimir Vasilev ^{3,*}, Malgorzata I. Szynkowska ^{1,*} and Pawel Mierczynski ^{1,*}

¹ Institute of General and Ecological Chemistry, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland; natalia.stepinska1996@gmail.com (N.S.); waldemar.maniukiewicz@p.lodz.pl (W.M.); jacek.rogowski@p.lodz.pl (J.R.)

² The Australian Wine Research Institute, Waite Precinct, Hartley Grove cnr Paratoo Road, Urrbrae (Adelaide), P.O. Box 197, Glen Osmond, Adelaide, SA 5064, Australia; agnieszka.mierczynska-vasilev@awri.com.au

³ School of Engineering, University of South Australia, Mawson Lakes, Adelaide, SA 5095, Australia

* Correspondence: m.mosinska@op.pl (M.M.); krasimir.vasilev@unisa.edu.au (K.V.); malgorzata.szynkowska@p.lodz.pl (M.I.S.); pawel.mierczynski@p.lodz.pl (P.M.); Tel.: +48-42-631-31-25 (M.M. & P.M.); +48-42-631-30-99 (M.I.S.)

Received: 21 January 2020; Accepted: 20 February 2020; Published: 1 March 2020

Abstract: In this work, bimetallic Cu-Ni catalysts supported on binary oxides containing ZnO, ZrO₂, CeO₂ and Al₂O₃ were investigated in hydrogen production via the oxidative steam reforming of methanol (OSRM). Their physicochemical properties were extensively studied using various methods such as BET, TPR-H₂, TPD-NH₃, XRD, SEM-EDS, ToF-SIMS and XPS. The reactivity measurements showed that the active phase and support composition played an important role in the activity of the catalyst in the OSRM. The most active system at higher temperatures was 30% Cu–10% Ni/CeO₂·Al₂O₃, with high catalytic activity attributed to the Cu_{0.8}Ni_{0.2} alloy formation. In addition, the reactivity results showed that the most active catalyst exhibited high acidity and was easily reduced. At low temperatures, the best catalytic properties were exhibited by 30% Cu–10% Ni/ZrO₂·Al₂O₃. The reactivity and physicochemical properties of the studied catalysts confirmed the crucial role of alloy composition on their catalytic properties in the oxy-steam reforming of methanol. The obtained results validate the possibility of using Cu-Ni catalysts for hydrogen production.

Keywords: hydrogen production; oxy-steam reforming of methanol; ZnO·Al₂O₃; ZrO₂·Al₂O₃; CeO₂·Al₂O₃; binary oxide; bimetallic catalysts; nickel catalyst; copper catalyst; OSRM

1. Introduction

Today, the awareness and concerns regarding environmental pollution and greenhouse emissions are at their highest level. This is a result of the progress of civilization and greater access to information. A most important problem remains the burning of traditional fossil fuels, which is the main source of not only carbon dioxide, but also of other dangerous atmospheric pollutants such as nitrogen oxides, sulphur oxides and carbon monoxide. Furthermore, the resources of fossil fuels are running out, which increases their prices but also causes increasing concerns regarding the economic future of countries dependent on exporting these raw materials. Therefore, there is a need to develop more effective and environmentally friendly energy sources. The use of alternative fuels is one solution to reduce fossil fuel consumption. For this reason, intense work is underway to become independent from oil extraction. One of the cheapest, most interesting and eco-friendly environmental fuels is hydrogen, which can be obtained from the process of methanol reforming [1]. Hydrogen has a number of advantages

and therefore is used in various fields in the energy sector, in fuel cell technology and electronics [2]. Currently, the oxidative steam reforming of methanol is one of the most common hydrogen production processes. It is well established that methanol is an excellent source for hydrogen generation because of the high hydrogen content. In addition, methanol has no C–C bonds, so it is easily reformed, does not require preliminary purification and it is easy to store. Moreover, the oxidative steam reforming of methanol process (OSRM) is an energetically favored process which can run in the auto-thermal way, without any external heat. Additional advantage of the OSRM is possibility to be carried out at low temperature range 150–330 °C without the carbon deposits formation [3–5]. OSRM reaction runs as per the following equation (Equation (1)):

One of the biggest advantages of liquid organic compound is their applicability for hydrogen production in portable systems. However, the reforming of methanol reaction requires to use the selective and stable catalyst under process conditions. It is well documented that copper and nickel based catalytic systems are the most often used catalytic material for the hydrogen production processes [4]. The synergistic interaction between metal and metal in a bimetallic system improves the catalytic and physicochemical properties of these systems compared to monometallic catalysts. Additionally, the bimetallic metal-Ni catalysts are intensively investigated and used in hydrogen production technologies. An important advantage of nickel-supported catalysts is their low cost [6,7]. It is reported the significant impact of copper addition to the nickel supported catalyst which improves the reducibility of these systems [8,9]. López et al. [10] investigated the Cu–Ni catalysts supported on ZrO₂ prepared by sequential and co-impregnation methods. They tested the catalytic activity of these systems in OSRM and claimed that the bimetallic Cu/Ni/ZrO₂ and Ni/Cu/ZrO₂ systems synthesized by subsequent impregnation method exhibited higher reactivity compared to monometallic systems and bimetallic alternatives obtained by simultaneous impregnation method. Perez-Hernandez et al. [11] also studied monometallic Cu/ZrO₂, Ni/ZrO₂ and bimetallic Cu–Ni/ZrO₂ catalysts in OSRM reaction. They reported that the presence of copper in the bimetallic Cu–Ni/ZrO₂ catalyst facilitates the reduction in nickel oxide species. The Cu–Ni/ZrO₂ system exhibited the highest catalytic activity at lower reaction temperatures compare to the investigated monometallic catalysts. Tahay et al. [12] investigated Cu, Cu–Ni, Ru, and Pt catalysts supported on TiO₂/monolith used in H₂ generation in SRM reaction. The BET measurement showed that the Specific Surface Area (SSA) of the catalysts increased by the co-impregnation of Ni and Cu which resulted in improvement of the methanol conversion value. The bimetallic Cu–Ni/TiO₂/monolith showed higher activity value of methanol conversion and lower CO selectivity compared to Cu/TiO₂/monolith catalysts. There authors also suggest that the Cu–Ni catalysts are economically favourable as an alternative for noble catalyst systems. It is also well-known that the Ni/Al₂O₃ catalyst is widely used in the OSRM reaction. The Al₂O₃ oxide is commonly added to the support of the catalysts to improve their mechanical strength and prevents the sintering of the catalyst [1]. The aluminium oxide is known for its large surface area and contributes to a strong interaction between the metal and the support. However, this feature can also have a negative impact on the activity of nickel catalysts supported on Al₂O₃. Therefore, the addition of various oxides to Al₂O₃ support of the catalysts are widely studied to optimize the catalyst support composition. For example, the addition of zirconium oxide to nickel catalyst systems leads to an increase in its stability, improves nickel dispersion and neutralize of the acidity of the catalyst surface. The catalytic systems containing ZrO₂ in the support system exhibited high efficiency towards the hydrogen production in OSRM reaction [13,14]. Cerium oxide are commonly used as a support material. It has been proven that CeO₂ improves the active phase dispersion and the catalyst reactivity. The catalysts supported on CeO₂ oxide exhibit good reduction behaviour because of high oxygen transfer capacity [15–17]. Promotion of the nickel catalysts by CeO₂ reduces the interaction between NiO and support making them easier to reduce and improves nickel dispersion. CeO₂ addition to nickel catalyst also has a

promotional effect on catalytic activity, stability and reduces the deposition of carbon [18]. Furthermore, the addition of ZnO oxide to the Al_2O_3 support increases the specific surface area of the system and thereby their reactivity in the studied reaction [19]. Gunter et al. [20] investigated the redox behaviour of the CuO/ZnO catalyst in the Steam Reforming of Methanol (SRM) reaction and reported that the interaction between Cu and ZnO has a significant effect on the catalytic properties of this system. Additionally, the zinc oxide improves the copper dispersion on the support surface. ZnO is not just a support but also catalytically active surface of the Cu/ZnO catalyst.

The purpose of the presented work was to develop cheap and efficient catalytic systems operating in the oxidative steam reforming of methanol process. Based on previous investigations, we decided to prepare bimetallic copper–nickel supported catalysts instead of copper or nickel catalysts promoted by noble elements [21–25]. Copper and nickel catalysts are much cheaper and are characterized by high activity and selectivity in OSRM [5,21,25,26]. Therefore, from the economics point of view, we chose Cu–Ni catalysts supported on binary oxides: $\text{ZnO} \cdot \text{Al}_2\text{O}_3$, $\text{CeO}_2 \cdot \text{Al}_2\text{O}_3$, $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3$. We selected the Zn : Al, Ce : Al and Zr : Al molar ratio equal 1:2 in these carriers because a higher content of aluminium oxide lead to a greater BET surface area and the higher catalytic activity of these systems in the OSRM reaction. The physicochemical properties of the catalytic systems developed in this work were comprehensively studies involving the following techniques: TPD- NH_3 (Temperature Programmed Desorption of NH_3), TPR- H_2 (Temperature Programmed Reduction using Hydrogen as a reducing agent), XRD (X-ray diffraction), BET (low temperature nitrogen adsorption), SEM-EDS (Scanning Electron Microscopy with an Energy Dispersive Spectrometer), ToF-SIMS (time-of-flight secondary ion mass spectrometry) and XPS (X-ray photoelectron spectroscopy). In addition, the correlation between the physicochemical properties and reactivity of the investigated catalyst in the OSRM process is described.

2. Results and Discussion

The main objective of this research was to optimize the composition of the catalyst for the highest efficiency in the process of methanol reforming with oxidative steam reforming. The catalytic properties of the investigated catalysts in the OSRM process were studied and correlated with their physicochemical properties and reactivity (see Table 1 and Figures 1–4). The catalytic tests were done at 120, 160, 200 and 250 °C. The catalytic activity measurements in the OSRM were performed using reduction at 300 °C for 1 h in a mixture of 5% of H_2 in argon (95%) mixture. The obtained results have been expressed as conversion of methanol, hydrogen yield and selectivity towards carbon monoxide and carbon dioxide. The results of the activity measurements performed in OSRM showed that the value of methanol conversion increases with increasing reaction temperature (see Figure 1). Firstly, we studied the activity of $x \text{ Cu} - y \text{ Ni}$ (where $x, y = 10, 20$ and 30 wt.%) catalysts supported on $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3$ binary oxide system in order to choose the proper content of copper to nickel in the active phase composition. In the case of these three catalysts, we observed that systems containing 30 wt.% of Cu and 10 wt.% of Ni exhibited the highest methanol conversion and hydrogen yield production. Additionally, the 30% Cu–10% Ni/ $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3$ catalyst showed the lowest selectivity to CO formation compared to other tested catalysts supported on $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3$ carrier. Based on the above measurements, the most optimal composition of the bimetallic catalysts in the catalyst systems supported on the $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3$ binary oxide was 30% Cu and 10% Ni, respectively. In the next step we decided to investigate the influence of the support composition on the reactivity results in OSRM process. Therefore 30% Cu–10% Ni catalysts supported on $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ and $\text{CeO}_2 \cdot \text{Al}_2\text{O}_3$ binary oxide systems were prepared and tested in OSRM reaction. The catalytic activity measurements performed for 30% Cu–10% Ni bimetallic catalysts showed that all these catalysts exhibited 100% methanol conversion at 250 °C. At a lower temperature (200 °C), the 30% Cu–10% Ni/ $\text{CeO}_2 \cdot \text{Al}_2\text{O}_3$ catalyst showed the highest value of methanol conversion (96%). It is worth noting that 30% Cu–10% Ni/ $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3$ catalyst exhibited the highest hydrogen yield and the highest methanol conversion at 160 °C. However, the 30% Cu–10% Ni/ $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3$ catalyst exhibited lower selectivity to CO_2 production and higher selectivity toward

CO formation compared to the 30% Cu–10% Ni/CeO₂·Al₂O₃ and 30% Cu–10% Ni/ZnO·Al₂O₃ systems. DME was not formed during the OSRM reaction in any of the investigated catalyst systems [21]. Lopez et al. [10] also investigated Cu–Ni/ZrO₂ catalysts prepared via co-impregnation and subsequent impregnation methods and tested in the OSRM process. The reactivity results of the monometallic and bimetallic systems followed the trend $Ni_{shell}Cu_{core}/ZrO_2 \approx Cu_{shell}Ni_{core}/ZrO_2 > Ni/Cu/ZrO_2 > Cu/Ni/ZrO_2 > Cu-Ni/ZrO_2 > Cu/ZrO_2 > Ni/ZrO_2$. These findings indicate that the bimetallic catalysts prepared by successive impregnation and co-impregnation methods show a higher reactivity than the monometallic Cu and Ni system obtained by impregnation method. In addition, the selectivity toward H₂ production was higher for the bimetallic catalysts. Perez-Hernandez et al. [27] investigated the catalytic activity in autothermal steam reforming of methanol process carried out on support ZrO₂ and bimetallic x Ni/Cu/ZrO₂ catalysts, where x = 3, 15 and 30 wt.%, respectively. The activity tests of these catalyst systems were performed in temperature range 200–400 °C. All investigated catalyst systems exhibited higher methanol conversion than the ZrO₂ support alone. An increase in Ni/Cu content in the catalyst composition of up to the 30 wt.% lead to a proportional increase in the methanol conversion value. It should be mentioned that at 250 °C they obtained 5% of CH₃OH conversion value for all investigated catalysts. The increase in the reaction temperature to 400 °C improved of the CH₃OH conversion value above 80%. They also determined the selectivity towards hydrogen production of investigated bimetallic Ni/Cu/ZrO₂ catalysts. The H₂ selectivity increased with an increase in the reaction temperature as the bimetallic x-Ni/Cu/ZrO₂ catalyst reach x loading value of 15 wt.%. The 30% Ni/Cu/ZrO₂ catalyst exhibits the methanol conversion value close to 3% Ni/Cu/ZrO₂ catalyst system. The most active catalytic system (15% Ni/Cu/ZrO₂) showed the H₂ yield equal 0.85 and 95% selectivity toward CO production at 400 °C.

Table 1. Results of the oxidative steam reforming process for calcined bimetallic catalysts.

Catalyst	Temp. (°C)	CH ₃ OH conv. (%)	H ₂ Yield	CO Selectivity (%)	CO ₂ Selectivity (%)
10% Cu–30%Ni/ ZrO ₂ ·Al ₂ O ₃	120	9	3.0	0	100.0
	160	22	3.0	0	100.0
	200	85	2.2	48	52.0
	250	98	2.1	68	32.0
20% Cu–20%Ni/ ZrO ₂ ·Al ₂ O ₃	120	14	3.0	0	100.0
	160	35	3.0	0	100.0
	200	86	2.0	48	52.0
	250	100	2.1	67.9	32.1
30% Cu–10%Ni/ ZrO ₂ ·Al ₂ O ₃	120	5	3.0	0	100.0
	160	79	3.0	0	100.0
	200	91	2.3	38.9	61.1
	250	100	3.0	33.4	66.6
30% Cu–10% Ni/ CeO ₂ ·Al ₂ O ₃	120	10	3.0	0	100.0
	160	26	3.0	0	100.0
	200	96	2.1	30.3	69.7
	250	100	2.2	27.0	73.0
30% Cu–10% Ni/ ZnO·Al ₂ O ₃	120	8	3.0	0	100.0
	160	19	3.0	0	100.0
	200	87	2.3	23.1	76.9
	250	100	2.1	30	70.0

Figure 1. The influence of the reaction temperature on the methanol conversion in the oxidative steam reforming of methanol (OSRM) process.

Figure 2. The influence of the reaction temperature of bimetallic catalysts on yield of hydrogen production in the OSRM process.

Figure 3. The influence of the reaction temperature of bimetallic catalysts on the selectivity towards CO₂ formation in the OSRM process.

Figure 4. The influence of the reaction temperature of bimetallic catalysts on the selectivity towards CO formation in the OSRM process.

Summarizing the activity measurements conducted in the oxidative steam reforming of methanol over a series of the Cu-Ni catalysts, we believe that the OSRM process follows the reaction mechanism postulated in the literature. According to the postulated mechanism oxidation of methanol take place via partial oxidation or steam reforming of methanol. Subsequently the oxidative steam reforming of methanol continues through the decomposition of CH₃OH and water gas shift reactions. In addition, the steam reforming of methanol can be represented as a combination of methanol decomposition reaction (DM) and water-gas shift reaction (WGS). Based on our reactivity results we have observed that at 120 and 160 °C the process runs according to the steam reforming process as evidenced by the hydrogen yield and CO₂ produced over various Cu-Ni bimetallic catalysts. It is also important that CO was not formed at low temperature, so WGS and decomposition reactions are not running. Increasing the temperature up to 200 °C leads to the formation of CO which is formed via the decomposition of methanol and can be consumed in water gas shift reaction as evidenced by the increased selectivity towards hydrogen production. We have observed the increase in the hydrogen yield for the selected catalysts (30% Cu–10% Ni/ZrO₂·Al₂O₃, 30% Cu–10% Ni/CeO₂·Al₂O₃). However, the increase in hydrogen selectivity in the case of 30% Cu–10% Ni/ZrO₂·Al₂O₃ system did not occur in parallel with the increase in selectivity towards CO₂ formation and the simultaneous decrease in the amount of carbon monoxide formed during the process. The observed result for this system could be explained by the possibility of carbon deposit formation during the catalytic process or/and trace amount of organics products formation like dimethyl ether.

In the next stage of this study, we determined the physicochemical properties of the investigated systems in order to correlate them with their catalytic activity in the OSRM process. The values of the specific surface area (SSA), monolayer capacity and average pore radius for all investigated supports and Cu-Ni catalysts are shown in Table 2. The results of the SSA measurements showed that the ZrO₂·Al₂O₃ and ZnO·Al₂O₃ supports had the same values of BET surface area and monolayer capacity equal 252 m²/g and 57.9 cm³/g, respectively. In the case of the CeO₂·Al₂O₃ system, the values of the monolayer capacity and the specific surface area were significantly lower compared to other tested supports. In addition, all tested catalyst systems had average pore size in the range 2–2.5 nm. Introduction of copper and nickel oxides onto the support surface results in decrease in the specific surface area. This can be explained by the blocking of the support pores by the metal oxide phase introduced during the preparation process. Concerning the x Cu–y Ni/ZrO₂·Al₂O₃ (where x (y) = 10, 20 and 30 wt.%) catalysts, the values of the BET surface area are in the range 119–142 m²/g. Furthermore, 20% Cu–20% Ni/ZrO₂·Al₂O₃ catalyst was distinguished by significantly higher values of the SSA and monolayer capacity of 142 m²/g and 32.7 cm³/g, respectively. On the

other hand, the SSA measurements obtained for 30% Cu–10% Ni catalysts supported on $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$, $\text{ZnO}\cdot\text{Al}_2\text{O}_3$ and $\text{CeO}_2\cdot\text{Al}_2\text{O}_3$ allow to present the BET surface area and monolayer capacity of the catalysts by the following order: 30% Cu–10% Ni/ $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3 \approx 30\%$ Cu–10% Ni/ $\text{CeO}_2\cdot\text{Al}_2\text{O}_3 > 30\%$ Cu–10% Ni/ $\text{ZnO}\cdot\text{Al}_2\text{O}_3$. It is worth mentioning, that 30% Cu–10% Ni/ $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ and 30% Cu–10% Ni/ $\text{CeO}_2\cdot\text{Al}_2\text{O}_3$ catalysts which exhibited similar BET surface area and monolayer capacity values were the most active catalyst systems in OSRM reaction. However, the 30% Cu–10% Ni/ $\text{CeO}_2\cdot\text{Al}_2\text{O}_3$ catalyst has the average pore radius equal to 2 nm.

Table 2. The specific surface area of calcined supports and bimetallic Cu–Ni catalysts.

Material	BET Surface Area (m^2/g)	Monolayer Capacity (cm^3/g)	Average Pore Radius (nm)
$\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$	252	57.9	2.5
$\text{CeO}_2\cdot\text{Al}_2\text{O}_3$	170	40.0	2.1
$\text{ZnO}\cdot\text{Al}_2\text{O}_3$	252	57.8	2
10% Cu–30% Ni/ $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$	120	27.6	2.5
20% Cu–20% Ni/ $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$	142	32.7	2.5
30% Cu–10% Ni/ $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$	119	27.3	2.5
30% Cu–10% Ni/ $\text{CeO}_2\cdot\text{Al}_2\text{O}_3$	120	27.7	2
30% Cu–10% Ni/ $\text{ZnO}\cdot\text{Al}_2\text{O}_3$	150	34.4	2.5

It is well documented in the scientific literature [28] that in the OSRM process, the acid centres play an important role because they are stabilising the intermediate products formed on the catalyst surface during the process. The amount and the rate of the formed intermediates such as formate, carbonate and methoxy species have crucial impact on the catalytic reactivity of the investigated catalysts in the investigated reaction. Therefore, in order to determine the relationship between the acidity of the catalyst systems and their activity in the oxidative steam reforming of methanol, we studied the acidic properties of the catalysts using the temperature-programmed desorption of ammonia (TPD- NH_3) technique. The acidity results obtained for the catalytic material are given on Table 3. The TPD- NH_3 obtained for the tested samples results confirmed the presence of weak, medium and strong acid centres detected for the investigated catalytic materials. The highest value of total acidity equal to 1.36 mmol/g had the $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ system. On the other hand, $\text{CeO}_2\cdot\text{Al}_2\text{O}_3$ showed the lowest total acidity of 0.33. In the case of the $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ system, we observed a higher quantity of medium and strong acid centers. Whereas, the $\text{CeO}_2\cdot\text{Al}_2\text{O}_3$ and $\text{ZnO}\cdot\text{Al}_2\text{O}_3$ supports were characterized by equal amount of each type of acid centers. The introduction of copper and nickel into the support surface results in slight increase in total acidity in the case of 30% Cu–10% Ni/ $\text{CeO}_2\cdot\text{Al}_2\text{O}_3$ and 30% Cu–10% Ni/ $\text{ZnO}\cdot\text{Al}_2\text{O}_3$ systems and significant decrease in this value for the x Cu–y Ni/ $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ (where x (y) = 10, 20 and 30 wt.%) catalysts. Additionally, in the case of x Cu–y Ni/ $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ (where x (y) = 10, 20 and 30 wt.%) catalyst systems, the TPD- NH_3 results showed that the total acidity decreases with an increase in the copper and a reduction in the nickel content. It is also worth mentioning that an increase in the copper content (decrease the nickel content) in the catalytic system leads to an increase in the weak and decrease in the medium and strong acid centers located on the catalytic material surface. Considering the 30% Cu–10% Ni catalysts supported on $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$, $\text{ZnO}\cdot\text{Al}_2\text{O}_3$ and $\text{CeO}_2\cdot\text{Al}_2\text{O}_3$, the values of the total acidity are in the range 0.57–0.68 mmol/g. The obtained catalytic activity results showed that the reactivity of the studied systems depend on their acidity and the strength of the acidic centres present on the surface. These results are very interesting because the 30% Cu–10% Ni/ $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ and 30% Cu–10% Ni/ $\text{CeO}_2\cdot\text{Al}_2\text{O}_3$ catalysts were characterized by the highest and lowest value of the total acidity, respectively. However, both catalyst systems exhibited the highest activity in the oxy-steam

reforming of methanol reaction at high temperature (200 and 250 °C). Furthermore, the highest content of weak acid centres (0.34 mmol/g) had the 30% Cu–10% Ni/ZrO₂·Al₂O₃ system, which exhibited the highest methanol conversion at 160 °C. This results confirm that these acid centres take part in a stabilization process of the intermediates over investigated bimetallic supported catalysts created during the reaction [25]. However, 30% Cu–10% Ni/CeO₂·Al₂O₃ and 30% Cu–10% Ni/ZnO·Al₂O₃ catalysts had the lower value of weak and the same values of medium and strong acid sites. These results showed practically the same activity in the studied temperature range and indicate that in the case of these catalysts, the acid centres are also an important factor which determine their activity in the OSRM process.

Table 3. TPD-NH₃ measurements of calcined supports and bimetallic Cu-Ni catalysts.

Catalytic Systems	Total Acidity (mmol/g)	Weak Centers (mmol/g)	Medium Centers (mmol/g)	Strong Centers (mmol/g)
	100–600 °C	100–300 °C	300–450 °C	450–600 °C
ZrO ₂ ·Al ₂ O ₃	1.36	0.25	0.46	0.65
CeO ₂ ·Al ₂ O ₃	0.33	0.10	0.10	0.13
ZnO·Al ₂ O ₃	0.62	0.24	0.19	0.20
10% Cu–30% Ni/ ZrO ₂ ·Al ₂ O ₃	0.67	0.30	0.24	0.13
20% Cu–20% Ni/ ZrO ₂ ·Al ₂ O ₃	0.60	0.31	0.21	0.08
30% Cu–10% Ni/ ZrO ₂ ·Al ₂ O ₃	0.57	0.34	0.20	0.03
30% Cu–10% Ni/ CeO ₂ ·Al ₂ O ₃	0.68	0.17	0.32	0.19
30% Cu–10% Ni/ ZnO·Al ₂ O ₃	0.67	0.22	0.28	0.17

The reduction behaviour of Cu-Ni supported catalysts was studied using the temperature-programmed reduction (TPR-H₂) technique. This technique is suitable for determining the interaction between the active phase and binary oxide components of the synthesized catalysts. The reduction profiles of the studied catalyst systems are given in Figures 5 and 6. The hydrogen reduction profile recorded for 10% Cu–30% Ni/ZrO₂·Al₂O₃ catalysts showed unresolved reduction steps in the temperature range 210–800 °C with a maximum of the hydrogen consumption rate located at about 170, 300, 400 and 580 °C, respectively. The first and second reduction effect are assigned to the reduction in copper (II) oxide according to the following steps: Cu²⁺ → Cu⁺ → Cu⁰. The third reduction effect is attributed to the reduction in free NiO species. The reduction peak located in temperature range 450–800 °C is attributed to NiO strongly interacted with the support components. The reduction profiles recorded for the 20% Cu–20% Ni/ZrO₂·Al₂O₃ catalyst showed partially resolved reduction peaks located in the temperature range of 180–390 °C with maximum hydrogen consumption peaks located at about 210, 260 and 300 °C, respectively. The first two reduction effects are connected with the reduction in copper (II) oxide to metallic copper via Cu₂O species and the third reduction effect is associated with the reduction in free nickel (II) oxide species. In the case of 20% Cu–20% Ni/ZrO₂·Al₂O₃ catalyst, we also observed high temperature peak situated at above 650 °C which is assigned to the reduction in NiAl₂O₄ spinel structure. Considering the TPR-H₂ profile recorded for the 30% Cu–10% Ni/ZrO₂·Al₂O₃ catalyst, partially resolved reduction effects in the temperature range 190–400 °C were also recorded. These results indicate that an increase in the copper content of the studied catalyst facilitates its reduction, leading to a shift of the reduction effects toward lower temperatures. The maximum H₂ consumption peaks are located at 220, 270, 310 °C. The reduction effects are connected with the two steps reduction in CuO to metallic Cu and with the reduction in NiO interacted with the support. The last high temperature reduction stage visible above 410 °C is assigned to the reduction nickel (II) oxide interacted with the support oxide. Next, reduction studies of 30% Cu–10% Ni catalysts

supported on $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3$, $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ and $\text{CeO}_2 \cdot \text{Al}_2\text{O}_3$ were performed. TPR profiles recorded for these catalytic systems are given in Figure 6. The hydrogen consumption profile recorded for 30% Cu–10% Ni/ $\text{CeO}_2 \cdot \text{Al}_2\text{O}_3$ catalyst also presented unresolved reduction peaks in the low temperature range of 140–330 °C associated with the two stage reduction in CuO crystallite species to metallic copper according to the stages: $\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$ and with the reduction in free NiO species. However, the TPR- H_2 profile recorded for the 30% Cu–10% Ni/ $\text{CeO}_2 \cdot \text{Al}_2\text{O}_3$ catalyst showed additional reduction steps located in the temperature range of 400 – 600 °C, which are assigned to the reduction in the surface oxygen species from the cerium (IV) oxide ($\text{CeO}_2 \rightarrow \text{CeO}_{2-x}$) and a high temperature peak centred in the temperature range of 800–900 °C assigned to bulk CeO_2 reduction process ($\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3$) [29]. Furthermore, the reduction effects observed for 30% Cu–10% Ni/ $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3$ were shifted toward a higher temperature range. Lopez et al. [10] studied the reducibility of the Cu–Ni/ ZrO_2 catalysts prepared by co-impregnation and subsequent impregnation methods. They reported that the reduction stage assigned to the ZrO_2 reduction was not observed at the studied temperature. The reduction effects observed for monometallic Ni/ ZrO_2 and Cu/ ZrO_2 catalysts were shifted to low temperatures compared to bimetallic Cu–Ni catalyst systems. In addition, the bimetallic catalysts promoted the active phase dispersion on the catalyst surface, but also facilitated the reducibility of the CuO and NiO species by modifying the active phase and support interaction. The TPR profile recorded for Cu–Ni/ ZrO_2 catalyst prepared using the co-impregnation method presented an unresolved reduction effect in the temperature range 170–320 °C. These reduction stages were assigned to the reduction in copper species highly disperse in the low temperature range and the reduction in NiO in low interaction with ZrO_2 support in the high temperature range. In previous studies for Cu–Ni/ ZrO_2 , the systems were also tested in OSRM reaction [11]. It was reported that the addition of Cu causes a spillover effect of hydrogen onto Ni. This induces a simultaneous reduction in CuO and NiO species and causes a shift of the reduction in the active phase to low temperatures. Vizcaino et al. [24] studied Cu–Ni catalyst supported on $\gamma\text{-Al}_2\text{O}_3$ oxide prepared by incipient wetness impregnation method. The TPR profile recorded for these systems showed two main broad reduction peaks observed in the temperature range: 160–260 °C and 320–550 °C. These effects present various interactions between the metal and the support components that depend on the carrier nature. The reduction peak visible at low temperature corresponds to the CuO reduction, whereas the peak at higher temperatures can be assigned to a NiO reduction. The facile reduction in NiO is explained by the synergistic effect which taking place between metallic Cu and metallic oxide (NiO) phases. In addition, the occurrence of CuO next to NiO leads to a decrease in both phases of their crystallite size. This behaviour can be explained by the characteristic property of the elements in group 11 of the periodic table. Their addition to nickel catalysts causes the easier reduction in NiO. Perez-Hernandez et al. [27] investigated the reduction properties of Ni/Cu/ ZrO_2 catalysts where the loading of Ni was 3, 15 and 30 wt.% of Ni/Cu (20% Ni/80% Cu), respectively. The TPR profiles of these three bimetallic catalysts with the TPR profiles were compared to their monometallic equivalents. This studied reduction behaviour showed that the reduction peaks observed in both Ni/ ZrO_2 and Cu/ ZrO_2 were modified in the case of bimetallic Ni/Cu/ ZrO_2 catalysts. The reduction effects were shifted to low temperatures when Ni and Cu were together in catalyst composition. The authors reported that, in the case of the bimetallic systems, a higher dispersion of the NiO species on the catalyst surface was observed and also improved the reducibility of CuO and NiO species by modifying the interaction between the active phase and the support. The TPR- H_2 profiles recorded for the bimetallic catalysts showed a hydrogen consumption peak close to 230 °C, which can be associated with the reduction in the CuO species highly dispersed on the ZrO_2 support and reduction peak assigned to NiO reduction, which ends at about 430 °C.

In order to explain the differences in activity of the investigated catalysts we studied their phase composition after calcination in an air atmosphere at 400 °C for 4 h and after reduction in a 5% H_2 in argon mixture at 300 °C for 1 h and following in the OSRM process. X-ray diffraction curves are given in Figures 7 and 8. The phase composition studies were carried out to determine the changes of the phase composition after various treatments and in order to elucidate the specific interaction between an

active phase component and the support. X-ray diffraction curves recorded for the bimetallic catalysts supported on $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ after calcination confirmed the amorphous nature of the ZrO_2 (positioned at 2θ angle: $30\text{--}35^\circ$), CuO (positioned at 2θ angle: $35.8^\circ, 39.0^\circ, 49.2^\circ, 58.7^\circ, 61.9^\circ, 66.7^\circ, 68.4^\circ, 75.5^\circ$) and NiO (positioned at 2θ angle: $37.4^\circ, 44.1^\circ, 53.5^\circ, 62.7^\circ, 79.3^\circ$) phases (see Figure 7). While, in the case of the bimetallic system supported on the $\text{ZnO}\cdot\text{Al}_2\text{O}_3$ system, the same crystallographic phases of CuO (positioned at 2θ angle: $35.8^\circ, 39.0^\circ, 49.2^\circ, 58.7^\circ, 61.9^\circ, 66.7^\circ, 68.4^\circ, 75.5^\circ$) and NiO (positioned at 2θ angle: $37.4^\circ, 44.1^\circ, 53.5^\circ, 62.7^\circ, 79.3^\circ$) were visible. In addition, the ZnAl_2O_4 (positioned at 2θ angle: 66.6°) phase was also detected in the diffraction curve recorded for this system. XRD spectra of bimetallic Cu-Ni system supported on $\text{CeO}_2\cdot\text{Al}_2\text{O}_3$ confirmed only the presence of CuO and NiO phases. Meanwhile, the diffraction curves of the catalyst systems being after reduction and reaction showed peaks that can be assigned to ZnAl_2O_4 (positioned at 2θ angle: 66.6°), metallic Ni (positioned at 2θ angle: $44.5^\circ, 51.6^\circ, 75.8^\circ$) and NiO (positioned at 2θ angle: 37.4°) phases (see Figure 8). It is worth mentioning that on the XRD pattern of the spent catalysts, peaks attributed to $\text{Cu}_{0.8}\text{Ni}_{0.2}$ (positioned at 2θ angle: $43.6^\circ, 50.9^\circ, 74.4^\circ$) were observed for the systems supported on $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ with low content of Ni (20% wt. of Ni) and for bimetallic system containing $\text{CeO}_2\cdot\text{Al}_2\text{O}_3$ as a catalytic support. Furthermore, CuNi (positioned at 2θ angle: $43.9^\circ, 51.8^\circ, 76.0^\circ$) alloys phase was detected only for the 30% Cu–10% Ni/ $\text{ZnO}\cdot\text{Al}_2\text{O}_3$ catalyst. Only in the case of the 10% Cu–30% Ni/ $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ catalyst were metallic Ni and NiO phases visible in the diffraction pattern. In addition, the diffraction peaks assigned to the NiO phases presented in the XRD patterns confirmed the partial reduction in nickel species on the surface of the investigated catalysts after the reduction and reaction processes. It is worth noting that the lack of diffraction peaks which could be assigned to the metallic Cu phase also confirmed Cu-Ni alloy formation in the case of the 10% Cu–30% Ni/ $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ catalyst. An additional confirmation of the copper-nickel alloy formation is the diagram in Figure 8 for the 30% Cu–10% Ni/ $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ catalyst. The visible XRD peak positioned at an about 43.5° 2θ angle which is shifted compared to pure metallic Ni or Cu phase, has confirmed $\text{Cu}_{0.8}\text{Ni}_{0.2}$ alloy formation. On the other hand, the lack of the diffraction peak which is attributed to the CuO phase confirmed that the copper(II) oxide present on the catalyst surface was totally reduced in the studied condition (in a mixture of 5% H_2 –95% Ar at 300°C for 1 h and reaction performed in OSRM process). In addition, the lack of metallic Cu and/or Ni particles in the diffraction patterns recorded for bimetallic catalysts may be also explained by the too small size of the crystallites to detect by the diffractometer [21,30]. The presence of other phases in the diffraction patterns were not confirmed by the X-ray diffraction technique. Hailong Liu et al. [31] investigated the phase composition of reduced monometallic 90Cu-SiO₂ and bimetallic 10Ni80Cu-SiO₂ catalysts before reaction and after 5 cycles in xylitol hydrogenolysis. The XRD patterns recorded for the investigated catalysts demonstrated characteristic diffraction peaks attributed to Cu^0 and Cu-Ni alloy and lack of formation the separate diffraction peak assigned to Ni^0 phase. The authors also reported that the crystallite size of Cu-Ni alloy of the freshly reduced 10Ni80Cu-SiO₂ catalyst slightly increased from 9.3 nm to 13.0 nm after utilizing this catalyst in 5 cycles while the Cu^0 crystallite size for the 90 Cu-SiO₂ system increased rapidly from 11.8 to 25.4 nm after the same procedure. These results indicate that the addition of Ni to the Cu-SiO₂ catalyst increased the stability of the system during the xylitol hydrogenolysis process due to the formation of stable Cu-Ni alloy. Lytkina et al. [32] studied Ni-Cu catalysts supported on ZrO_2 prepared by subsequent impregnation method. The synthesized catalysts were also characterized by X-ray diffraction method. The XRD patterns recorded for bimetallic catalysts supported on an amorphous ZrO_2 and reduced in a stream of H_2 and Ar at 350°C for 3 h showed diffraction reflexes attributed to the metals dominating in a catalyst composition, i.e., Cu and Ni. X-ray diffraction curves also clearly demonstrate diffraction peaks shifted towards to the 2θ angle value, corresponding to the peak of metal with higher content in catalyst composition which indicate alloy formation.

Figure 5. Temperature programmed reduction curves of calcined bimetallic systems (400 °C for 4 h in an air atmosphere) x Cu– y Ni/ $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3$ (where x (y) = 10, 20 and 30 wt.%).

Figure 6. Temperature programmed reduction curves of calcined 30% Cu–10% Ni bimetallic catalysts supported on $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3$, $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ and $\text{CeO}_2 \cdot \text{Al}_2\text{O}_3$ (400 °C for 4 h in an air atmosphere).

Figure 7. X-ray diffraction curves of various bimetallic catalysts calcined at 400 °C for 4 h in an air atmosphere.

In the next stage of our study, the morphology of the selected catalytic materials was investigated. Scanning electron microscope with an energy dispersive spectrometer (EDS) detector was a useful tool used for this purpose. The results were given as SEM images and EDS spectra, which were collected for the studied supports and catalysts and are presented on Figures 9–11, respectively. Figure 9 shows the scanning electron microscopy images of the supports. The presented results confirm rather homogenous distributions of the elements included in the composition of each catalytic material. The results of the SEM-EDS measurements of calcined bimetallic catalysts are shown in Figure 11. The EDS

spectra and SEM images clearly confirmed the elemental composition of the studied bimetallic catalytic materials. The obtained results support the presence of copper, nickel, aluminium and oxygen on the surfaces of all the investigated bimetallic catalysts, while elements such as cerium, zinc and zirconium were visible only for the selected supported catalysts. Figure 10 shows the EDS spectrum of the surface of the $x\text{ Cu}-y\text{ Ni}/\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ (where $x(y) = 10, 20$ and $30\text{ wt.}\%$) catalysts. The obtained results clearly indicate that the intensity of the diffraction reflects corresponding to copper and nickel depends on the content of these elements on the catalysts surface. The presented EDS spectra confirmed that the highest concentration of copper on the investigated surface was detected for the catalyst with the highest copper content (see Figure 10). In addition, the system with the highest copper content on the surface of the investigated catalysts also displayed the highest activity in the investigated reaction process.

In order to characterize the chemical composition of the surface of the reduced catalyst, time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements were performed. Emission intensities of the selected positive secondary ions collected from the surface of the investigated catalysts are given in Table 4. The number of counts of Cu^+ and Ni^+ ions emitted from the catalyst surface were chosen for the qualitative analysis of the concentration of these metals on the catalyst surface. In the case of $x\text{ Cu}-y\text{ Ni}/\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ (where $x(y) = 10, 20$ and $30\text{ wt.}\%$) catalysts, the relationship between the activity in OSRM reaction and the relative value of emission intensity of Cu^+ ions to emission intensity of Ni^+ ions from the catalyst surface were determined. The highest value of this intensity ratio (equal 1.96) was found for the most active $30\% \text{ Cu}-10\% \text{ Ni}/\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ catalyst in the OSRM process. The emission of the CuNi^+ ions from the catalyst surface confirmed the formation of CuNi alloy, which may explain the high activity of the investigated catalyst systems. Moreover, the presence of CuAlO^+ and NiAlO^+ ion peaks in TOF-SIMS spectra of the catalysts indicate the interaction between the active phase and the support. Similarly, the emission of ZrAlO^+ ions from catalyst supported on $\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$ binary oxide confirms the occurrence of the specific interactions between alumina and zirconium oxide. While, in the case of $30\% \text{ Cu}-10\% \text{ Ni}$ catalysts supported on various binary oxides ($\text{ZrO}_2\cdot\text{Al}_2\text{O}_3$, $\text{ZnO}\cdot\text{Al}_2\text{O}_3$ and $\text{CeO}_2\cdot\text{Al}_2\text{O}_3$), the highest activity in the oxy–steam reforming of methanol was measured for the catalyst with the lowest emission of Ni^+ secondary ions. These observations resonate with the XRD and EDS results obtained for the bimetallic supported catalysts and agree well with our previous findings.

Figure 8. X-ray diffraction curves of various bimetallic catalysts reduced in $5\% \text{ H}_2$ – $95\% \text{ Ar}$ mixture at 300°C for 1 h and tested in OSRM process.

Figure 9. SEM images of calcined supports in an air atmosphere at 400 °C for 4 h.

Figure 10. Scanning electron microscope images and EDS spectra collected for the investigated bimetallic $x\text{Cu}-y\text{Ni}/\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3$ catalysts (where $x(y) = 10, 20$ and 30 wt.%).

Figure 11. Scanning electron microscope images of all investigated calcined bimetallic systems.

The state and nature of active phase components present on the surface of the investigated catalytic material was also examined using the XPS technique. XPS measurements were done for the selected calcined and reduced systems, and the results are given in Figure 12. The high resolution XPS spectra of Cu $2p_{3/2}$ with the fitted curves of the Cu catalysts after calcination and reduction show characteristic peaks in the range 925–963 eV. The XPS spectra indicate the existence of copper species on the first and second oxidation states [23,33,34] on the catalyst surface. Fitting of the spectra confirms the reduction process of the Cu^{2+} species to metallic Cu^0 and Cu^+ species (see Table 5). In addition, the satellite peaks [35] of all the spectra of all the samples confirmed the occurrence of various interactions between the Cu^{2+} species and other components of the investigated systems. It should be highlighted that the shifts of the characteristic binding energy of Cu^0/Cu^+ species towards lower values indicate the possible alloying process, which takes place between metallic copper and nickel. The formation of this alloy was already confirmed by XRD and ToF-SIMS measurements and discussed above.

Table 4. The intensity of the selected secondary ions identified on the surface of the investigated bimetallic catalysts reduced in a mixture of 5% H₂–95% Ar at 300 °C for 1 h.

		Number of Counts $\times 10^3$														
		Cu ⁺	Ni ⁺	NiO ⁺	CuOH ⁺	NiOH ⁺	CuNi ⁺	CuNiO ⁺	CuNiOH ⁺	NiCe ⁺	CuAl ⁺	CuAlO ⁺	NiAlO ⁺	CuAlOH ⁺	NiAlOH ⁺	ZrAlO ⁺
Catalysts	10% Cu–30% Ni/ ZrO ₂ ·Al ₂ O ₃	174.8	115.6	0.6	1.3	5.8	4.8	9.1	15.1	-	-	1.1	1.0	2.7	1.8	6.2
	20% Cu–20% Ni/ ZrO ₂ ·Al ₂ O ₃	153.3	98.9	0.5	1.3	5.2	4.0	7.6	12.1	-	1.0	1.7	1.0	3.3	1.9	5.6
	30% Cu–10% Ni/ ZrO ₂ ·Al ₂ O ₃	220.3	112.6	0.6	1.9	6.6	4.2	7.6	12.7	-	1.4	3.9	1.5	5.2	2.0	6.2
	30% Cu–10% Ni/ CeO ₂ ·Al ₂ O ₃	118.3	89.5	0.5	1.0	4.3	3.0	5.2	6.6	0.4	0.4	0.9	1.3	2.5	1.5	-
	30% Cu–10% Ni/ ZnO·Al ₂ O ₃	232.4	156.1	0.9	1.7	8.2	5.0	8.7	12.2	-	0.9	1.6	2.3	4.5	3.2	-

Figure 12. XPS spectra of (a) Cu 2p for various calcined Cu-Ni systems, (b) Cu 2p of various Cu-Ni catalysts reduced at 300 °C in a mixture of 5% H₂ in argon.

Table 5. Atomic percentages of copper species Cu²⁺, Cu⁺ and Cu⁰ on the surface of the investigated calcined and reduced catalysts.

After Reduction at 300 °C			After Calcination at 400 °C		
Sample	Cu/Cu ⁺ (%) (932.3 eV)	Cu ²⁺ (%) (934.3 eV)	Sample	Cu/Cu ⁺ (%) (932.3 eV)	Cu ²⁺ (%) (934.3 eV)
30% Cu–10% Ni/ ZrO ₂ ·Al ₂ O ₃	67.4	32.6	30% Cu–10% Ni/ ZrO ₂ ·Al ₂ O ₃	61.9	38.1
30% Cu–10% Ni/ CeO ₂ ·Al ₂ O ₃	65.9	34.1	30% Cu–10% Ni/ CeO ₂ ·Al ₂ O ₃	52.4	47.6
30% Cu–10% Ni/ ZnO·Al ₂ O ₃	69.7	30.3	30% Cu–10% Ni/ ZnO·Al ₂ O ₃	64.4	35.5

3. Experimental

3.1. Catalyst Synthesis

The support oxides (ZnO·Al₂O₃, CeO₂·Al₂O₃, ZrO₂·Al₂O₃) have been synthesized using the co-precipitation method. During the preparation of the supports, an aqueous solution of appreciate 1 mol/L zinc or zirconium or cerium nitrate and 1 mol/L aluminium nitrate were mixed in appreciate quantity under vigorous stirring at 80 °C. In the next step, a precipitate was formed using a concentrated ammonia solution which was added by dropwise addition until the pH of the solution reached values between 10 and 11. The obtained precipitates were washed using deionised water. Then, the obtained precipitates were dried at 120 °C for 12 h and calcined in an air atmosphere for 4 h at 400 °C. Whereas the bimetallic systems Cu-Ni were synthesized using the wet co-impregnation method. The final bimetallic x Cu–y Ni catalysts contained the Ni and Cu with the following concentrations x, y = 10%, 20%, and 30% copper and nickel, respectively. To achieve the appropriate amount of nickel and copper Ni(NO₃)₃·6H₂O and Cu(NO₃)₂·3H₂O were used as a precursors of metals. The final catalysts system was dried in an air atmosphere for 2 h at 120 °C and calcined for 4 h at 400 °C.

3.2. Catalyst Characterisation

The specific surface area and porosity of catalytic materials were studied using the BET method based on low temperature ($-196\text{ }^{\circ}\text{C}$) nitrogen adsorption in a Sorptomatic 1900 Carlo-Erba apparatus. The temperature programmed reduction (TPR- H_2) investigations were done using AMI-1 system in the temperature range of $25\text{--}900\text{ }^{\circ}\text{C}$ with a linear heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ [26,36]. A consumption of hydrogen was monitored using thermal conductivity (TCD) detector (Altamira Instruments, Pittsburgh, PA, USA). The acidity of the investigated catalysts were studied using temperature programmed desorption (TPD- NH_3) method [37]. Phase composition of the catalytic material was investigated by X-ray diffraction technique. The detailed description of this method can be found in our previous work [38]. The surface morphology of the synthesized catalyst systems was determined using an S-4700 scanning electron microscope HITACHI (S-4700 HITACHI, Tokyo, Japan) with EDS detector (Energy Dispersive Spectrometer) (ThermoNoran, Madison, WI, USA). ToF-SIMS mass spectra of ions were obtained using a ToF-SIMS IV (ION-ToF GmbH, Münster, Germany) secondary ion mass spectrometer equipped with a high mass resolution time-of-flight analyser. In each experiment, a Bi^{3+} primary ion gun was used. The sample surface area of approximately $500\text{ }\mu\text{m} \times 500\text{ }\mu\text{m}$ ($100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ for tablets) was recorded for the secondary ions mass spectra. In each experiment, an analysed area was irradiated with the pulses of 25 keV Bi^{3+} ions at 10 kHz repetition rate and an average ion current 0.38 pA during 30 s , giving an ion dose below static limit of $1 \times 10^{13}\text{ ions cm}^{-2}$. The oxidation state of the active phase component was investigated using X-ray photoelectron spectroscopy. XPS spectra were recorded on an AXIS Ultra DLD (Kratos Analytical, Manchester, UK) equipped with a monochromatic Al K α radiation source ($h\nu$, 1486.6 eV) at a power of 225 W using Mg K α radiation source ($h\nu = 1253.6\text{ eV}$). High resolution spectra were collected for selected photoelectron peaks at a pass energy of 20 eV in order to identify the chemical state of each element. C1s neutral carbon peak at 285 eV was used as a reference signal for all the binding energies (BEs). The latest version of CASA XPS software (version 2.3.19, Casa Software Ltd., Teignmouth, UK) was applied to the processing and component fitting of the high-resolution spectra.

3.3. Catalytic Test

Reactivity tests in OSRM process were carried out under atmospheric pressure using a flow fixed bed reactor. The process was carried out in the temperature range $120\text{--}250\text{ }^{\circ}\text{C}$. In each experiment, the catalyst load was about 0.2 g and the reaction mixture composition was following: $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{O}_2 = 1:1:0.4$ (molar ratio) and the GHSV was $26,700\text{ h}^{-1}$. The analyses of the obtained products were performed using GC analysis (a description of chromatographic analysis was presented in our previous work [21,26]). The selectivity values of the obtained products were calculated based on following equations presented below:

$$\text{Methanol conversion (\%)} = \frac{n_{\text{in}} \text{CH}_3\text{OH} - n_{\text{out}} \text{CH}_3\text{OH}}{n_{\text{in}} \text{CH}_3\text{OH}} \cdot 100\%$$

$$\text{H}_2 \text{ Yield} = \frac{n_{\text{out}} \text{H}_2}{n_{\text{in}} \text{CH}_3\text{OH} - n_{\text{out}} \text{CH}_3\text{OH}}$$

$$\text{CO selectivity (\%)} = \frac{n_{\text{out}} \text{CO}}{n_{\text{out}} \text{CO}_2 + n_{\text{out}} \text{CO}} \cdot 100\%$$

$$\text{CO}_2 \text{ selectivity (\%)} = \frac{n_{\text{out}} \text{CO}_2}{n_{\text{out}} \text{CO}_2 + n_{\text{out}} \text{CO}} \cdot 100\%$$

where,

$n_{\text{out}} \text{H}_2$ —mole of H_2 in the feed out,

$n_{\text{out}} \text{CO}_2$ —mole of CO_2 in the feed out,

$n_{\text{out}} \text{CO}$ —mole of CO in the feed out,

n_{in} CH₃OH—mole of CH₃OH in the feed in,

n_{out} CH₃OH—mole of CH₃OH in in the feed out,

4. Conclusions

In the present study, the bimetallic x Cu– y Ni (where x (y) = 10, 20 and 30 wt.%) catalysts supported on binary oxides (ZnO·Al₂O₃, CeO₂·Al₂O₃, ZrO₂·Al₂O₃) were prepared via the conventional wet impregnation method. The hydrogen production via OSRM process was effectively carried out over a series of Cu–Ni catalyst systems. Their physicochemical properties were studied using BET, TPR-H₂, TPD-NH₃, XRD, ToF-SIMS, XPS and SEM-EDS techniques. Their properties have been correlated with reactivity in the studied OSRM reaction. The most active system at 160 °C was the 30% Cu–10% Ni/ZrO₂·Al₂O₃ catalyst. The high reactivity of this catalyst is explained by the alloy formation of Cu_{0.8}Ni_{0.2}—confirmed using the XRD, ToF-SIMS and XPS techniques. In addition, the most active system at 200 °C was the 30% Cu–10% Ni/CeO₂·Al₂O₃ catalyst, which was easily reducible and owing to a Cu_{0.8}Ni_{0.2} alloy on its surface. On the other hand, the composition of an alloy is also important parameter influencing the reactivity of the Cu–Ni catalysts in the studied process. A bimetallic 30% Cu–10% Ni/ZnO·Al₂O₃ catalyst containing the equimolar alloy Cu–Ni and the irreducible carrier demonstrated the lowest activity in the studied process. The catalytic activity measurements indicate, that the Cu–Ni bimetallic catalysts may be the future catalytic systems applied for hydrogen generation in mobile devices based on fuel cells.

Author Contributions: The results presented in the work were designed and presented by M.M., N.S., J.R., W.M., K.V., A.M.-V., M.I.S. and P.M. All authors have read and agreed to the published version of the manuscript.

Funding: This work was partially funded by the Lodz University of Technology for the scholarship (Fundusz Młodych Naukowców na Wydziale Chemicznym PŁ programme, No. W-3D/FMN/2G/2017). Magdalena Mosinska thanks the Lodz University of Technology for a scholarship (Własny Fundusz Stypendialny PŁ programme, No. RNN/WFS/25/2018).

Acknowledgments: This work was also partially funded by the National Science Centre within the “OPUS” Programme, Poland (Grant No. 2018/29/B/ST8/01317).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Madej-Lachowska, M. Kinetic studies on steam reforming of methanol over Cu/Zn/Zr/Ce/Cr catalyst. *Przemysł Chem.* **2016**, *1*, 151–154. [[CrossRef](#)]
2. Dutta, S. A review on production, storage of hydrogen and its utilization as an energy resource. *J. Ind. Eng. Chem.* **2014**, *20*, 1148–1156. [[CrossRef](#)]
3. Zhang, X.; Chan, S.H.; Ho, H.K.; Tan, S.-C.; Li, M.; Li, G.; Li, J.; Feng, Z. Towards a smart energy network: The roles of fuel/electrolysis cells and technological perspectives. *Int. J. Hydrogen Energy* **2015**, *40*, 6866–6919. [[CrossRef](#)]
4. Pérez-Hernández, R.; Mondragón-Galicia, G.; Maravilla, A.A.; Palacios, J. Nano-dimensional CeO₂ nanorods for high Ni loading catalysts: H₂ production by autothermal steam reforming of methanol reaction. *Phys. Chem. Chem. Phys.* **2013**, *15*, 12702. [[CrossRef](#)] [[PubMed](#)]
5. Mierczynski, P.; Mosinska, M.; Zakrzewski, M.; Dawid, B.; Ciesielski, R.; Maniecki, T.; Maniukiewicz, W. Influence of the Zn–Al binary oxide composition on the physicochemical and catalytic properties of Ni catalysts in the oxy-steam reforming of methanol. *React. Kinet. Mech. Catal.* **2017**, *121*, 453–472. [[CrossRef](#)]
6. LeValley, T.L.; Richard, A.R.; Fan, M. The progress in water gas shift and steam reforming hydrogen production technologies—A review. *Int. J. Hydrogen Energy* **2014**, *39*, 16983–17000. [[CrossRef](#)]
7. Wang, Z.; Wang, C.; Chen, S.; Liu, Y. Co–Ni bimetal catalyst supported on perovskite-type oxide for steam reforming of ethanol to produce hydrogen. *Int. J. Hydrogen Energy* **2014**, *39*, 5644–5652. [[CrossRef](#)]
8. Biswas, P.; Kunzru, D. Steam reforming of ethanol on Ni–CeO₂–ZrO₂ catalysts: Effect of doping with copper, cobalt and calcium. *Catal. Lett.* **2007**, *118*, 36–49. [[CrossRef](#)]

9. Cunha, A.F.; Wu, Y.; Li, P.; Yu, J.-G.; Rodrigues, A.E. Sorption-Enhanced Steam Reforming of Ethanol on a Novel K–Ni–Cu–Hydrotalcite Hybrid Material. *Ind. Eng. Chem. Res.* **2014**, *53*, 3842–3853. [\[CrossRef\]](#)
10. Lopez, P.; Mondragón-Galicia, G.; Espinosa-Pesqueira, M.; Mendoza-Anaya, D.; Fernández, M.; Gómez-Cortés, A.; Bonifacio, J.; Martínez-Barrera, G.; Pérez-Hernández, R. Hydrogen production from oxidative steam reforming of methanol: Effect of the Cu and Ni impregnation on ZrO₂ and their molecular simulation studies. *Int. J. Hydrogen Energy* **2012**, *37*, 9018–9027. [\[CrossRef\]](#)
11. Pérez-Hernández, R.; Galicia, G.M.; Anaya, D.M.; Palacios, J.; Ángeles-Chávez, C.; Arenas-Alatorre, J. Synthesis and characterization of bimetallic Cu–Ni/ZrO₂ nanocatalysts: H₂ production by oxidative steam reforming of methanol. *Int. J. Hydrogen Energy* **2008**, *33*, 4569–4576. [\[CrossRef\]](#)
12. Tahay, P.; Khani, Y.; Jabari, M.; Bahadoran, F.; Safari, N. Highly porous monolith/TiO₂ supported Cu, Cu–Ni, Ru, and Pt catalysts in methanol steam reforming process for H₂ generation. *Appl. Catal. A Gen.* **2018**, *554*, 44–53. [\[CrossRef\]](#)
13. Velu, S.; Suzuki, K.; Okazaki, M.; Kapoor, M.; Osaki, T.; Ohashi, F. Oxidative Steam Reforming of Methanol over CuZnAl(Zr)-Oxide Catalysts for the Selective Production of Hydrogen for Fuel Cells: Catalyst Characterization and Performance Evaluation. *J. Catal.* **2000**, *194*, 373–384. [\[CrossRef\]](#)
14. Sanchez-Sanchez, M.; Yerga, R.N.; Fierro, J. Ethanol steam reforming over Ni/MxOyNi/MxOy–Al₂O₃ (M=Ce, La, Zr and Mg) catalysts: Influence of support on the hydrogen production. *Int. J. Hydrogen Energy* **2007**, *32*, 1462–1471. [\[CrossRef\]](#)
15. Men, Y.; Gnaser, H.; Zapf, R.; Hessel, V.; Ziegler, C. Parallel screening of Cu/CeO₂/γ-Al₂O₃ catalysts for steam reforming of methanol in a 10-channel micro-structured reactor. *Catal. Commun.* **2004**, *5*, 671–675. [\[CrossRef\]](#)
16. Men, Y.; Gnaser, H.; Ziegler, C.; Zapf, R.; Hessel, V.; Kolb, G. Characterization of Cu/CeO₂/γ-Al₂O₃ Thin Film Catalysts by Thermal Desorption Spectroscopy. *Catal. Lett.* **2005**, *105*, 35–40. [\[CrossRef\]](#)
17. Liu, Y.; Hayakawa, T.; Suzuki, K.; Hamakawa, S.; Tsunoda, T.; Ishii, T.; Kumagai, M. Highly active copper/ceria catalysts for steam reforming of methanol. *Appl. Catal. A Gen.* **2002**, *223*, 137–145. [\[CrossRef\]](#)
18. Wang, S.; Lu, G.Q.; Millar, G.J. Carbon Dioxide Reforming of Methane To Produce Synthesis Gas over Metal-Supported Catalysts: State of the Art. *Energy Fuels* **1996**, *10*, 896–904. [\[CrossRef\]](#)
19. Jensen, J.; Johannessen, T.; Wedel, S.; Livbjerg, H. Preparation of ZnO–Al₂O₃ Particles in a Premixed Flame. *J. Nanoparticle Res.* **2000**, *2*, 363–373. [\[CrossRef\]](#)
20. Günter, M.; Ressler, T.; Jentoft, R.; Bems, B. Redox Behavior of Copper Oxide/Zinc Oxide Catalysts in the Steam Reforming of Methanol Studied by in Situ X-Ray Diffraction and Absorption Spectroscopy. *J. Catal.* **2001**, *203*, 133–149. [\[CrossRef\]](#)
21. Mierczynski, P.; Mosinska, M.; Maniukiewicz, W.; Nowosielska, M.; Czyrkowska, A.; Szyrkowska, M.I. Oxy-steam reforming of methanol on copper catalysts. *React. Kinet. Mech. Catal.* **2019**, *127*, 857–874. [\[CrossRef\]](#)
22. Mierczynski, P.; Ciesielski, R.; Kedziora, A.; Nowosielska, M.; Kubicki, J.; Maniukiewicz, W.; Czyrkowska, A.; Maniecki, T. Monometallic copper catalysts supported on multi-walled carbon nanotubes for the oxy-steam reforming of methanol. *React. Kinet. Mech. Catal.* **2015**, *117*, 675–691. [\[CrossRef\]](#)
23. Mierczynski, P.; Vasilev, K.; Mierczynska, A.; Maniukiewicz, W.; Szyrkowska, M.I.; Maniecki, T.P. Bimetallic Au–Cu, Au–Ni catalysts supported on MWCNTs for oxy-steam reforming of methanol. *Appl. Catal. B Environ.* **2016**, *185*, 281–294. [\[CrossRef\]](#)
24. Mierczynski, P. Comparative Studies of Bimetallic Ru–Cu, Rh–Cu, Ag–Cu, Ir–Cu Catalysts Supported on ZnO–Al₂O₃, ZrO₂–Al₂O₃ Systems. *Catal. Lett.* **2016**, *146*, 1825–1837. [\[CrossRef\]](#)
25. Mierczynski, P.; Mierczynska-Vasilev, A.; Ciesielski, R.; Mosinska, M.; Nowosielska, M.; Czyrkowska, A.; Maniukiewicz, W.; Szyrkowska, M.I.; Vasilev, K. High Active and Selective Ni/CeO₂–Al₂O₃ and Pd–Ni/CeO₂–Al₂O₃ Catalysts for Oxy-Steam Reforming of Methanol. *Catalysts* **2018**, *8*, 380. [\[CrossRef\]](#)
26. Mierczynski, P.; Mosinska, M.; Maniukiewicz, W.; Vasilev, K.; Szyrkowska, M.I. Novel Rh(Pd)–Cu(Ni) supported catalysts for oxy-steam reforming of methanol. *Arab. J. Chem.* **2020**, *13*, 3183–3195. [\[CrossRef\]](#)
27. Pérez-Hernández, R.; Gutiérrez-Martínez, A.; Espinosa-Pesqueira, M.; Estanislao, M.L.; Palacios, J. Effect of the bimetallic Ni/Cu loading on the ZrO₂ support for H₂ production in the autothermal steam reforming of methanol. *Catal. Today* **2015**, *250*, 166–172. [\[CrossRef\]](#)
28. Turco, M.; Bagnasco, G.; Cammarano, C.; Senese, P.; Costantino, U.; Sisani, M. Cu/ZnO/Al₂O₃ catalysts for oxidative steam reforming of methanol: The role of Cu and the dispersing oxide matrix. *Appl. Catal. B Environ.* **2007**, *77*, 46–57. [\[CrossRef\]](#)

29. Rynkowski, J.; Paryjczak, T.; Lewicki, A.; Szynkowska, M.I.; Maniecki, T.; Jóźwiak, W.K. Characterization of Ru/CeO₂-Al₂O₃ catalysts and their Performance in CO₂ Methanation. *React. Kinet. Catal. Lett.* **2000**, *71*, 55–64. [[CrossRef](#)]
30. Udani, P.; Gunawardana, P.; Lee, H.C.; Kim, D.H. Steam reforming and oxidative steam reforming of methanol over CuO–CeO₂ catalysts. *Int. J. Hydrogen Energy* **2009**, *34*, 7648–7655. [[CrossRef](#)]
31. Liu, H.; Huang, Z.; Kang, H.; Li, X.; Xia, C.; Chen, J.; Liu, H. Efficient bimetallic NiCu-SiO₂ catalysts for selective hydrogenolysis of xylitol to ethylene glycol and propylene glycol. *Appl. Catal. B Environ.* **2018**, *220*, 251–263. [[CrossRef](#)]
32. Lytkina, A.A.; Zhilyaeva, N.A.; Ermilova, M.; Orekhova, N.V.; Yaroslavl'tsev, A. Influence of the support structure and composition of Ni–Cu-based catalysts on hydrogen production by methanol steam reforming. *Int. J. Hydrogen Energy* **2015**, *40*, 9677–9684. [[CrossRef](#)]
33. Mierczynski, P.; Vasilev, K.; Mierczynska, A.; Maniukiewicz, W.; Maniecki, T. The Effect of ZnAl₂O₄ on the Performance of Cu/Zn_xAl_yO_{x+1.5y} Supported Catalysts in Steam Reforming of Methanol. *Top. Catal.* **2013**, *56*, 1015–1025. [[CrossRef](#)]
34. Kulkarni, G.; Rao, C.N.R. EXAFS and XPS Investigations of Cu/ZnO Catalysts and Their Interaction with CO and Methanol. *Top. Catal.* **2003**, *22*, 183–189. [[CrossRef](#)]
35. Ertl, G.; Hierl, R.; Knözinger, H.; Thiele, N.; Urbach, H. XPS study of copper aluminate catalysts. *Appl. Surf. Sci.* **1980**, *5*, 49–64. [[CrossRef](#)]
36. Maniecki, T.; Stadnichenko, A.I.; Maniukiewicz, W.; Bawolak, K.; Mierczynski, P.; Boronin, A.; Jozwiak, W.K. An active phase transformation on surface of Ni-Au/Al₂O₃ catalyst during partial oxidation of methane to synthesis gas. *Kinet. Catal.* **2010**, *51*, 573–578. [[CrossRef](#)]
37. Mierczynski, P.; Vasilev, K.; Mierczynska, A.; Maniukiewicz, W.; Ciesielski, R.; Rogowski, J.; Szynkowska, M.I.; Trifonov, A.Y.; Dubkov, S.V.; Gromov, D.G.; et al. The effect of gold on modern bimetallic Au–Cu/MWCNT catalysts for the oxy-steam reforming of methanol. *Catal. Sci. Technol.* **2016**, *6*, 4168–4183. [[CrossRef](#)]
38. Mierczynski, P.; Shtyka, O.; Kozanecki, M.; Filipczak, P.; Maniukiewicz, W.; Gromov, D.G.; Dubkov, S.V.; Sysa, A.; Trifonov, A.Y.; Czyłkowska, A.; et al. Effect of the AACVD based synthesis atmosphere on the structural properties of multi-walled carbon nanotubes. *Arab. J. Chem.* **2020**, *13*, 835–850. [[CrossRef](#)]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).