Article

Effect of Selected Factors on Catalytic Activity of Bimetallic Copper-Gold Catalysts in Selective Oxidation of Glycerol

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Abstract: A current problem in petrochemical industry is the elimination of crude glycerol which is the by-product of biodiesel production obtained during the transesterification of vegetable oils and animal fats. In this work are presented the results of characterisation of mesoporous ceria, zirconia and mixed cerium-zirconium oxide modified with gold and/or copper species and their application as catalysts in the selective oxidation of glycerol in the liquid phase. The characterisation of samples was performed using selected advanced techniques (ATR-FTIR, UV-vis, XRD, adsorption and desorption of nitrogen, XRD, XPS, TEM, SEM, STEM-EDXS). The obtained data show that the bimetallic Cu-Au systems supported on mesoporous ceria, zirconia or mixed cerium-zirconium oxide are more active and selective in glycerol oxidation to glycric acid in basic solution than acidic conditions. The data of HPLC analysis provided that glyceric acid was the first stable product in the liquid phase during the oxidation process in alkali media. It is worth noting that the bimetallic Cu-Au catalysts were characterised also by the catalytic stability, because the increase of selectivity to glyceric acid during the recycling of Cu-Au catalysts was achieved. The influence of selected factors (oxygen source, pH solution, oxygen pressure, base content and stirring speed) on the catalytic activity of Cu-Au catalysts will be presented and discussed.

Keywords: bimetallic catalysts; ceria; zirconia; cerium-zirconium oxides; gold; copper; glycerol oxidation; materials characterisation

1. Introduction

Glycerol is a chemical compound, which is produced during the transesterification of oils and fats [1,2]. The increase of biodiesel production has led to the surplus of crude glycerol which cannot be assimilated into traditional glycerol outlets. Glycerol is a highly functionalized reagent which can be applied for the production of valuable oxygenated fine chemicals, e.g. fuel sources, pharmaceuticals or biodegradable polymers [3-5]. Various catalytic ways can be applied to this aim: oxidation, hydrogenolysis, dehydration, etherification, transesterification, etc. [6]. The products of glycerol oxidation are the number of valuable chemical compounds, e.g.: glyceric acid, tartronic acid, 1,3-dihydroxyacetone or glyceraldehyde [7-10]. The challenge in the development of efficient catalysts for glycerol oxidation reaction is obtained the catalysts which will be characterised by high activity, selectivity to selected products and catalytic stability.

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The catalytic glycerol oxidation reaction has been conducted in the aqueous solution of glycerol at acidic or basic conditions, over the monometallic catalysts, e.g. modified with Au, Pd or Pt and the bimetallic, e.g. Pt-Au or Pd-Au catalysts [11,12]. Regardless of the supporting material, size and morphology of catalytic, metallic gold species, the oxidation of glycerol usually produces fairly high selectivity toward the formation of glyceric acid, and also in smaller concentration to other acids: tartronic acid, glycolic acid, oxalic acid or lactic acid [13,14]. Glyceric acid and its derivatives are promising fine chemicals for pharmaceutical or biochemical industry and there are used e.g. in the production of medicaments for ethanol and acetaldehyde oxidation [15]. Glyceric acid and its derivatives can be applied also in the synthesis of biodegradable surfactants, novel functionalized phospholipid derivatives and phosphatidylcholine analogues [16].

It has been reported [17] that the introduction of the second metal to the active phase of catalysts can induce the structural modifications of gold particles. Other factors of reaction conditions (pH, temperature, pressure and the use of an appropriate solvent) have influence on the catalytic activity and selectivity in alcohols oxidation [18-20]. It has been shown that the modification of gold catalysts by the addition of the second metal can improve the selectivity for certain products, because this metal plays the role of promotor and it can stabilize the metallic gold particles of bimetallic active phase. For example, it was reported that Au-Pd [21–27], Au-Pt [25,26] and Au-Cu [28,29] catalysts were characterised of a positive interaction between two metals and this interaction led to the growth of activity in oxidation processes and the catalytic stability of catalysts.

The main goal of this work is shown that the chemical composition of supports and their modification of copper species can lead to obtain the active catalysts in the reaction of glycerol oxidation at selected conditions and their activity and selectivity to value products can be controlled by many factors (oxygen source, pH solution, oxygen pressure, base content and stirring speed).

2. Results and discussion

2.1. General characterisation

Selected analytical techniques (XRD, adsorption and desorption of nitrogen, TEM, SEM, STEM-EDXS, XPS) were used to characterise the structure and texture properties of materials before and after their using as catalysts in the reaction of selective glycerol oxidation in alkali media. These studies were performed also to obtain the information about the chemical composition of catalysts after their reusing in the oxidation process and to estimate the oxidation state of metal species before their performance in glycerol oxidation. The discussion about the comparison of characterisation results is described in the paragraph titled „the changes in materials after reaction” (the point of 2.3 in this work) and the general information about the properties of calcined, fresh materials, before their using in the catalytic test will be presented in this paragraph.

XRD measurements were performed to obtain the information about the crystallinity of oxides, coordination of cerium and zirconium species and the estimation of metallic gold particles size. All studied oxides were crystal materials and the wide-angle XRD pattern (Fig. S1) of ceria was characteristic of the crystal cubic phase (ICPDS ICDD PDF Card – 00-043-1002). In the case of catalysts based on pure zirconia, zirconia was a mixture of the tetragonal (ICPDS ICDD PDF Card – 00-042-1164) and monoclinic phase (ICPDS ICDD PDF Card – 00-007-0343). The XRD pattern of CeZrO₃ revealed the domination of reflections due to the structure of zirconia. It can suggest that in this oxide, ceria was located in the structure of zirconia with a uniform distribution. The obtained
XRD patterns showed that the deposition of copper species on the surface of catalysts led to the appearance of the reflections which could be assigned to the crystal phase of metallic gold particles (the reflection at $\theta = \approx 38.2^\circ$).

The texture parameters were estimated using nitrogen adsorption and desorption isotherms (Fig. S2). The surface area of the catalysts depended on the nature of the supports and increased in the following order: CeO$_2$ (24 m$^2$ g$^{-1}$) < CeZrO$_x$ (103 m$^2$ g$^{-1}$) < ZrO$_2$ (121 m$^2$ g$^{-1}$). The modification of catalysts with gold and copper species only slightly decreased the surface area of monometallic oxide supports, whereas the catalysts based on CeZrO$_x$ revealed much lower surface area (about 65 m$^2$ g$^{-1}$) after their modification with copper and gold species. More details about the results of the texture parameters of catalysts before their using in glycerol oxidation were reported in earlier paper [30] and they were shown in this work to outline the general information about the morphology of materials.

SEM and TEM images (Fig. S3) were recorded for selected catalysts before and after their using as catalysts in glycerol oxidation at basic conditions at 333 K for 5 h. These images confirmed the presence of mesoporous in the bimetallic catalysts (Fig. S3, SEM image of CuAu/ZrO$_2$) and monometallic gold and/or bimetallic copper-gold particles on their surface (Fig. S3, TEM image of CuAu/ZrO$_2$). The study using TEM improved the positive effect of copper species addition on the decrease of metallic gold particles, because the modification of gold catalysts by the deposition of copper species led to obtain smaller gold particles, which size was around 2-5 nm.

### 2.2. The influence of selected conditions on the catalytic activity and selectivity

It has been reported in previous study [30-32] that high conversion rates for the oxidation of different alcohols can be achieved over the bimetallic copper-gold catalysts. In this work will be presented the selected aspects of reaction conditions (oxygen source, pH, pressure or solvent) which could have influence on the catalytic activity and selectivity of catalysts based on ceria, zirconia, cerium-zirconium oxides in the reaction of glycerol oxidation.

#### 2.2.1. The influence of oxygen source and pH solution

It was reported in the earlier work [30] that the bimetallic Cu-Au catalysts can achieve a high glycerol conversion (>70 %) in its oxidation at 333 K for 5 h and selectivity to glyceric acid (65-79 %), if the source of oxygen was pure oxygen. In this reaction other products were created in the liquid phase, e.g. glycolic acid and/or formic acid, but the selectivities to these reagents were much lower than the selectivity to glyceric acid. These products were obtained in the earlier studies [33-37].

The comparison of the results of glycerol oxidation over Cu-Au catalysts at basic conditions using gas oxygen or H$_2$O$_2$ (Fig. 1) as oxygen source shows that this parameter strongly influences on the catalytic activity of catalysts. It can be explained by the differences in the mechanism of hydrogen peroxide decomposition. It has been reported [38] that hydrogen peroxide can be used in the selected conditions as friendly oxidant for environmental, because it can decompose to water and molecular oxygen [2 H$_2$O$_2$ → 2 H$_2$O + O$_2$].

In the case of Cu-Au catalysts, the conversion of glycerol in its oxidation over these catalysts using the source of oxygen as hydrogen peroxide (glycerol conversion in the range of 31-47 %) was lower than when the source of oxygen was gas oxygen. Additionally, the reaction run to gases products (CO$_2$ and other gases) which could not analysed using HPLC device. The highest glycerol conversion in its oxidation by hydrogen peroxide was achieved over CuAu/CeZrO$_x$. It can improve the positive interaction between cerium and zirconium species based on the electron transfer
between oxygen from the crystal structure of oxides and cations of cerium (Ce³⁺ and Ce⁴⁺) and zirconium Zr⁴⁺. The possibility of the presence of these species was evidenced by the UV-vis and XPS study. The obtained results suggest that in the selective oxidation of glycerol to glyceric acid, the transport of oxygen and its form in aqua solution had influence on the rate and pathway of glycerol transformation. At acid conditions, glycerol conversion in its oxidation over Cu-Au catalysts was lower than in the basic conditions, because it was in the range of 16-28 %. It is worth to note, that in the case of CuAu/CeO₂, higher glycerol conversion in its oxidation was achieved in the presence of H₂O₂ (28 %), than in pure oxygen (18 %). Hydrogen peroxide is strong oxidant which can use in the oxidation of inorganic and organic compounds in the liquid-phase under very mild reaction conditions. The interaction between hydrogen peroxide and the surface of catalysts had influence on the transformation of glycerol molecules during their oxidation.

![Graph showing conversions and selectivities over selected bimetallic copper-gold catalysts in glycerol oxidation in the liquid phase in different conditions](image)

**Fig. 1.** Conversions and selectivities achieved over selected bimetallic copper-gold catalysts in glycerol oxidation in the liquid phase in different conditions (in the presence of pure oxygen or hydrogen peroxide and acid (HNO₃) or base (NaOH) in the reaction solution). Reaction conditions: 15.00 g of H₂O; molar ratio NaOH:glycerol = 2:1 (0.0030 mol of NaOH; 0.0015 mol of glycerol) or HNO₃:glycerol = 2:1 (0.0030 mol of HNO₃; 0.0015 mol of glycerol), 0.0300 g catalyst; 5 h at 1000 rpm. GLA means glyceric acid, GCA – glycolic acid, FA – formic acid, TA – tartronic acid, GLD – glyceraldehyde, LA – lactic acid.

Depending on the properties of catalyst surface, different types of O-O bond cleavage in H₂O₂ could occur (homolytic or heterolytic), and different types of oxidative species could be generated. The results of glycerol oxidation to glyceric acid suggest that it was a surface-catalysed process, but
the formation of this acid was possible mainly in the presence of base (NaOH) and pure oxygen (O₂) molecules. In the presence of H₂O₂, glycerol was oxidized to gasses products and glycerol conversion in its oxidation was lower. It can suggest that the directly introduction of hydrogen peroxide to the reaction mixture could lead to its reaction with a base (NaOH) and the oxidation of glycerol to carbon dioxide and/or other gases products.

Fig. 2. Conversions and selectivities achieved over selected bimetallic copper-gold catalysts in glycerol oxidation in the liquid phase at basic conditions and at different pressure of oxygen (3 or 6 bars). Reaction conditions: 15.00 g of H₂O; molar ratio NaOH:glycerol = 2:1 (0.0030 mol of NaOH; 0.0015 mol of glycerol) or HNO₃:glycerol = 2:1 (0.0030 mol of HNO₃; 0.0015 mol of glycerol), 0.0300 g catalyst; 5 h at 1000 rpm. GLA means glyceric acid, GCA – glycolic acid, FA – formic acid, TA – tartronic acid.

2.2.2. The effect of oxygen pressure

The influence of different oxygen pressure on the catalytic activity over Cu-Au catalysts was also investigated in the reaction of glycerol oxidation at 333 K for 5 h at 1000 rpm at basic conditions. The results, which were collected in Figure 2, show that the decrease of oxygen concentration used to glycerol oxidation (from 6 to 3 bars) leads to the decrease of conversion at 25-39 %. At lower oxygen pressure (3 bars), the selectivity to glyceric acid (for all Cu-Au catalysts) and glycolic acid (excluding CuAu/CeZrOₓ) decreases and it is observed the growth of selectivity to gases products. It is observed the positive effect of cerium-zirconium oxide on the increase of glycerol conversion and it can suggest the presence of the electron interaction between cerium and zirconium species, which can improve the catalytic properties of active phase (the bimetallic Cu-Au system) in the oxidation.
process, but lower oxygen content leads to the total oxidation of glycerol. The obtained results show that the increase of oxygen content in the autoclave can improve not only glycerol conversion in its oxidation, but also the selectivity to glyceric acid. The increase of oxygen pressure had positive effect on the increase of selectivity to glyceric acid, especially over catalysts based on cerium species. It can suggest that cerium species could lead to the growth of rate the adsorption of oxygen molecules on the surface of catalysts and the migration of oxygen to active centres (metallic gold particles).

![Conversion and selectivity for CuAu/CeO2, CuAu/CeZrOx, CuAu/ZrO2 catalysts](image)

**Fig. 3.** Conversions and selectivities achieved over selected bimetallic copper-gold catalysts in glycerol oxidation in the liquid phase at basic conditions and at different pressure of oxygen (3 or 6 bars). Reaction conditions: 15.00 g of H₂O; molar ratio NaOH:glycerol = 2:1 (0.0030 mol of NaOH; 0.0015 mol of glycerol) or HNO₃:glycerol = 2:1 (0.0030 mol of HNO₃; 0.0015 mol of glycerol), 0.0300 g catalyst; 5 h at 1000 rpm. GLA means glyceric acid, GCA – glycolic acid, FA – formic acid, TA – tartronic acid.

### 2.2.3. The effect of base concentration

The influence of base content in the reaction solution was studied for the Cu-Au catalysts in the oxidation of glycerol at 333 K for 5 h at 1000 rpm in the presence of pure oxygen (6 bars). The results in Figure 3 show that a base in aqua solution appears on glycerol conversion and selectivity to glyceric acid. It is worth to note, that in the case of CuAu/ZrO₂, the conversion of glycerol in its oxidation and the selectivity to glyceric acid did not change in the presence of lower NaOH content. It can suggest that the first step of this reaction – the dehydrogenation via H-abstraction of one of the primary OH groups of glycerol does not depend on base content in the reaction solution. In the case
of CuAu/CeO₂, the increase of conversion and the decrease of selectivity are observed when molar ratio between NaOH and glycerol is 1:1. It is observed also the growth of selectivity to formic acid and/or glycolic acid and the decrease of selectivity to glyceric acid at NaOH:glycerol = 1:1 (excluding CuAu/ZrO₂).

![Conversion and selectivities achieved over selected bimetallic copper-gold catalysts in glycerol oxidation in the liquid phase at basic conditions at different speed stirring (400, 800 or 1200 rpm).](image)

**Fig. 4.** Conversions and selectivities achieved over selected bimetallic copper-gold catalysts in glycerol oxidation in the liquid phase at basic conditions at different speed stirring (400, 800 or 1200 rpm).

### 2.2.4. The effect of stirring speed

The influence of stirring speed was studied for bimetallic copper-gold catalysts in basic conditions at selected speeds in the range of 400-1200 rpm (Table 1). The increase of speed from 400
to 1200 rpm led to the changes in the glycerol conversion in its oxidation over all bimetallic catalysts. The materials were characterised by the different chemical composition of supports and the specific surface area. The pore size of all Cu-Au catalysts were very similar, but specific pore area were significantly differs [30,32] and the effect of stirring speed was not the same for all of them (the increase in activity by ca. 18-40% from 400 to 1200 rpm). It can suggest that the growth of glycerol conversion with the increase in the stirring speed originated rather from the increase of diffusion rate in pores and the influence of products transport from solid to liquid was smaller, because in the case of catalysts which were characterised by small specific surface area – CuAu/CeO2 (24 m2 g-1), this growth was bigger (55 %), than in the case of bimetallic catalysts which surface area was above 60 m2 g-1 (28-39 %).

Table 1. The reuse of Cu-Au catalysts in glycerol oxidation at 333 K for 5 h at 1200 rpm in basic solution.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>conv., %</th>
<th>selectivity, %</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>1st</td>
<td>2nd</td>
</tr>
<tr>
<td>Au/CeO2</td>
<td>31</td>
<td>62</td>
</tr>
<tr>
<td>Au/CeZrOx</td>
<td>32</td>
<td>25</td>
</tr>
<tr>
<td>Au/ZrO2</td>
<td>19</td>
<td>35</td>
</tr>
<tr>
<td>CuAu/CeO2</td>
<td>79</td>
<td>79</td>
</tr>
<tr>
<td>CuAu/CeZrOx</td>
<td>85</td>
<td>73</td>
</tr>
<tr>
<td>CuAu/ZrO2</td>
<td>83</td>
<td>62</td>
</tr>
<tr>
<td>Cu/CeO2</td>
<td>27</td>
<td>22</td>
</tr>
<tr>
<td>Cu/CeZrOx</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>Cu/ZrO2</td>
<td>26</td>
<td>21</td>
</tr>
</tbody>
</table>

1 Reaction conditions: 15.000 g distilled water; NaOH:glycerol = 2:1; 0.0030 mol NaOH; 0.0015 mol glycerol; 0.0300 g catalyst; 5 h at 333 K at 1200 rpm; pO2 = 6 bars
2 GLA – glyceric acid, GCA – glycolic acid, FA – formic acid, TA – tartronic acid, LA – lactic acid

2.2.5. The catalytic stability

It was published in the literature [39,40] that gold catalysts supported on carbon or transition metal oxides can be used in glycerol oxidation several times without deactivation. It has been reported that the best stability in recycling tests in glycerol oxidation was achieved over gold loaded on carbon (greater than palladium or platinum on carbon catalysts), showing neither deactivation and metal leaching. The results of the reuse experiments for monometallic (gold or copper) and bimetallic (copper-gold) catalysts are shown in Table 1. It is worth emphasizing that each catalyst used in the first cycle of glycerol oxidation at 333 K for 5 h at 1200 rpm was simply recovered by decantation of the solvent after the reaction and then it was used in the second cycle without any washing and drying. The data in Table 1 present that the values of glycerol conversion of achieved over bimetallic catalysts changed a little after the second cycle of oxidation. It is worth noting that in the second cycle, higher selectivity to glyceric acid in glycerol oxidation was obtained
over Au/CeO₂ and bimetallic catalysts. And other side, the decreases in the activity can be ascribed
to the loss of catalyst during the workup.

2.3. The changes in materials after glycerol oxidation

The catalysts were studied before and after their application in glycerol oxidation using
UV-vis, AFT-FTIR, XRD, TEM and XPS. The order of these studies was evidenced the changes in
the structure of catalyst surface after glycerol molecules adsorption and their transformation during
the oxidation in the liquid phase.

2.3.1. UV-vis study

UV-vis spectroscopy is an analytical method which can be used for the estimation of the
oxidation state and the coordination of metals. In Figure 5 are shown the UV-vis spectra of
monometallic gold and bimetallic copper-gold catalysts before and after their drying at 383 K for 13
h, after their application in glycerol oxidation at 333 K for 5 h at basic conditions and their reusing in
this oxidation processes.

It is worth to note that the position of a band coming from ligand to metal charge transfer
depends on the ligand field symmetry surrounding cerium centre [41,42]. In the case of samples with
cerium species, the intense bands present in the range between 200 and 400 nm can be due to the
ligand-metal charge transfer (LMCT) between ligand and cerium cations. In the case of UV-vis spectra
recorded for the catalysts based on ceria, two bands are observed, the first at around 265 and the
second at around 350 nm. They are characteristic of the charge transfer from oxygen ion (O₂⁻) to
cerium cation (Ce⁴⁺). The UV-vis band at around 265 nm can be attributed to the LMCT for cerium
cation (Ce⁴⁺) which is the tetrahedral coordinated and the band at around 350 nm can be assigned to
cerium cation (Ce⁴⁺) which coordination number is higher than four.

The shape of the spectra recorded for CuAu/CeO₂ is similar to the shape of spectra performed
for Au/CeO₂, but the intensity of the bands are decreased. For CeZrOₓ support, the only one UV-vis
band at around 270 nm is visible with a shoulder at around 220 nm indicating that in the
ceria-zirconium mixed oxide the distribution of cerium oxidation states and the coordination of
cerium species on the surface are different from these observed in the catalysts based on pure ceria.

The range characteristic of the charge transfer between oxygen ions and cerium cations is also typical
of the charge transfer transitions of Au⁺ and Au⁺ ions with ligands [43-49] or for the absorption
bands due to the transition of electrons between molecular orbitals of the few-atomic clusters Auₙ (n
< 10). It can explain why, the examination of this region cannot be useful for characterisation of
cationic gold species. For the estimation of metallic gold particles, the range of 500-560 nm can be
applied. The bands in this region can be attributed to the optical absorption of light excited
oscillating conductivity electrons of metallic gold particles called plasmon resonance [50-54]. The band
around 540-560 nm can originate also from d-d electron transfer in metallic gold [52-54]. In the case of
UV-vis spectra recorded for calcined catalysts, before their drying, the band around 530-560 nm was
found only in UV-vis spectra recorded for the bimetallic (Au-Cu) catalysts (Fig. 5). After the drying
of the monometallic gold samples, this weak band was found also in the UV-vis spectra. The
application of the catalysts in the reaction of glycerol oxidation changed the intensity and the
position of these bands. It can improve the chemical reaction between glycerol oxidation products
and the metals from the catalysts during the oxidation process.
Fig. 5. The UV-vis spectra recorded for: [A] CuAu/CeO₂, [B] Au/CeO₂, [C] CuAu/CeZrOₓ, [D] Au/CeZrOₓ, [E] CuAu/ZrO₂ and [F] Au/ZrO₂, before (a, black line), after drying at 383 K for 13 h (b, red line), after the 1st cycle of glycerol oxidation (c, blue line) and after the 2nd cycle of glycerol oxidation (d, green line).

These bands became well visible also in the spectra of monometallic (Au) samples after the first cycle of oxidation and/or reusing of catalysts in the oxidation process. The obtained results of UV-vis study can evidence the changes of catalysts surfaces during glycerol. It is worth to note that the UV-vis bands due to plasmon resonance in gold nanoparticles are observed at around 530-560 nm and they achieved higher intensity in the UV-vis spectra recorded for the materials after their reusing as the catalysts of glycerol oxidation (excluding CuAu/CeO₂ after its using in the second cycle of reaction and CuAu/ZrO₂ after its application in glycerol oxidation). It can suggest the migration of
metallic gold species during glycerol oxidation in the liquid phase on the external surface in the case of monometallic gold catalysts. This phenomena was confirmed by XPS measurements and it can explain the increase of glycerol conversion in its oxidation, especially over Au/CeO₂ (Table 1). In the case of the UV-vis spectra of bimetallic copper-gold catalysts, the shoulder bands are seen around 650 nm, which can be attributed to different form of charge transfer, e.g.: LMCT in copper oxides nanoclusters [55,56], LMCT in (Cu - O - Cu)²⁺ clusters [57-59], inter-valence CT transitions between copper and other metal ions (gold, cerium and/or zirconium) in the bulk solid solution [60], 2E_g – 2T₂g transitions of Cu²⁺ ions in an octahedral O₆ configuration [57,58], polymeric Cu⁺ ··· O₂⁻ ··· Cu⁺ species [57-59].

The UV-vis results demonstrate the role of the composition of the support on the form of gold and copper species in mono- and bimetallic catalysts and they can improve the possibility of electron interaction between both metals.

![Fig. 6](https://example.com/fig6.png)

Fig. 6. The ATR-FTIR spectra of the selected samples: a) pure glycerol (black line), b) Au/CeZrOₓ (red line), c) Cu/CeZrOₓ (green line), d) CuAu/CeZrOₓ (blue line). The final spectra were created after the subtraction of spectra recorded for sample after glycerol oxidation at 333 K for 5 h in basic conditions at 1200 rpm and for fresh sample before oxidation of glycerol.

### 2.3.2. ATR-FTIR measurements

The ATR-FTIR spectra were carried out for the samples based on the cerium-zirconium oxides and pure glycerol (Fig. 6). The comparison of bands in the FTIR spectra of pure glycerol and the catalysts after their using in glycerol oxidation showed that the stretching vibration of C-H bonds in the intermediates as like methoxy species gave the similar positions of bands in the range (1450-750 cm⁻¹) in the case of monometallic (gold or copper) catalysts (Au/CeZrOₓ and Cu/CeZrOₓ). Any bands in the FTIR spectrum were seen in the case of the bimetallic (copper-gold) catalyst (CuAu/CeZrOₓ). It can suggest that the adsorption of glycerol molecules on the surface of CuAu/CeZrOₓ and their transformation to intermediates was faster than in the case of monometallic catalysts. This phenomenon can explain why glycerol conversions in its oxidation at 333 K for 5 h over monometallic catalysts were lower than analogues bimetallic catalysts, because the active sites...
were blocked by the products of the reaction adsorbed on the surface of catalysts. It shows that the
ATR-FTIR study of the catalysts after their application in glycerol oxidation can be effective method
to prove the adsorption and desorption of reagents on the surface of materials during the oxidation
processes.

2.3.3. XRD study

The XRD patterns of monometallic gold and bimetallic copper-gold catalysts were performed
not only for samples before, but also after their using in glycerol oxidation at 333 K for 5 h at basic
conditions (Fig. S1). The comparison of XRD patterns recorded for samples before and after their
performance in the oxidation process suggests that the conditions of reaction changed slightly the
crystal phase of materials, because the intensity and positions of reflections in the XRD patterns are
similar. It can explain the catalytic stability of catalysts in the second cycle of glycerol oxidation
(Table 1).

2.3.4. TEM and STEM-EDXS analysis

SEM image recorded for CuAu/ZrO2 (Fig. S3, left side) confirms the presence of mesopores in
the bimetallic catalyst (selected entrances to pores, which diameter is <10 nm, are circled red line).
TEM image of CuAu/ZrO2 (Fig. S3, right side) confirms the presence of metallic gold particles which
size is between 2 and 5 nm in the bimetallic catalyst. It can suggest that the addition of copper
species on the surface of gold catalysts leads to the protection of metallic gold particles by their
agglomeration during the reaction of oxidation. The positive effect of copper loading on the
stabilization of gold particles during the reaction of glycerol oxidation in alkali media was confirmed
by the STEM-EDXS study (Fig. S4). The STEM images confirmed the presence of bimetallic
copper-gold particles in CuAu/CeZrOx which the size is smaller than 10 nm after the performance of
catalyst in glycerol oxidation, but it is worth to note that individual bimetallic particles increased to
around 20 nm after the reaction. The EDX spectra (Fig. S4) show that the bimetallic copper-gold
particles are located mainly on the external surface of materials and the content of gold species in the
bulk of materials is much lower than copper species content. It can suggest the migration of copper
species during modification of materials using this metal and the strong interaction copper with the
support based on cerium-zirconium oxide.

2.3.5. XPS measurements

XPS method was used to estimate the oxidation state of gold, copper and cerium species in the
catalysts before and after their using in glycerol oxidation and their distribution on the external
surface (Figures S5 and S6, Tables 2, 3 and S1).

The composition of supports had influence on the changes in the position and intensity of bands
in XP spectra. In the monometallic gold catalysts before and after their using in the oxidation
process, gold species on the external surface were in the metallic (Au0) and cationic form (Au\(^{\delta+}\),
where \(\delta\) means Au\(^+\) or Au\(^3+\)), excluding Au/CeO\(_2\), because in this material gold was only in the form
of metallic gold particles (Table 2). The changes of gold distribution in all monometallic gold
catalysts were slightly and the domination form was metallic gold (Au\(^0\)). Cationic gold species (Au\(^{\delta+}\))
were formed on mixed cerium-zirconium oxide and pure zirconia in monometallic gold samples and
the part of cationic species were reduced to metallic form (Au\(^0\)) after the reaction of oxidation (Table
2). The reduction of small part of cationic gold (Au\(^{\delta+}\)) to metallic gold (Au\(^0\)) and cationic cerium
(from Ce\(^4+\) to Ce\(^3+\)) can suggest that the products of glycerol oxidation (CO\(_2\), other gases products
and/or glyceric acid) influenced on the partial reduction of gold and cerium species. In the case of
bimetallic copper-gold catalysts, the main form of gold was metallic gold (Au\(^0\)), but it is worth noting the appearance of metallic gold species with the partial negative charge on the external surface (Au\(^{δ-}\)) and the disappearance of cationic gold (Au\(^{δ^+}\)) species in CuAu/CeO\(_2\) after glycerol oxidation. However, the distribution of (Au\(^{δ-}\)) decreased after the reaction in the case of bimetallic catalysts with zirconium species. It means that (Au\(^{δ-}\)) is created on the external surface of ceria during the oxidation of glycerol, especially over the oxidized form of cerium (Ce\(^{4+}\)), because the addition of zirconium to the supports led to the bigger growth of reduced form of cerium species (Ce\(^{3+}\)) in the distribution of cerium species, especially after the reaction. It is interesting, because in CuAu/CeO\(_2\), the distribution of cerium species on the external surface before and after the reaction is very similar (23 % of cerium is in the reduced form before and 24 % after glycerol oxidation). In all oxides, cerium species in the oxidized form (Ce\(^{4+}\)) is a main form of cerium species (Table 2), but the presence of zirconium in mixed oxide has positive effect on the reduction of cerium species during the reaction of glycerol oxidation (e.g. in CuAu/CeZrO\(_x\), Ce\(^{3+}\) distribution increased from 19 to 38 %).

The modification with copper species had influence on the distribution of the reduced form of cerium species (Ce\(^{3+}\)) in bimetallic copper-gold catalysts, because it was lower than in the analogues monometallic gold catalysts before the application of materials in the oxidation of glycerol.

Generally, the presence of cerium and copper species led to the easier reduction of cationic gold in the catalysts before or after their using in the oxidation of glycerol than in the case of analogues monometallic catalysts. In the monometallic gold and bimetallic copper-gold materials, cationic gold was observed in the case of all catalysts before or after glycerol oxidation (excluding Au/CeO\(_2\)), but its distribution was in small quantities. The introduction of copper not only decreased cationic gold species (excluding CuAu/CeZrO\(_x\)), but it also increased the amount of metallic gold on supports with enhanced shielding of the core hole. This finding indicates that the existence of reducible copper species in copper-gold catalysts can be responsible for enhanced core-hole shielding [61].

Table 2. The distribution of gold, copper and cerium species in the selected monometallic gold and bimetallic copper-gold catalysts before and after their using in glycerol oxidation at 333 K for 5 h at 1200 rpm at basic conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Distribution (estimated using a XPS method), %</th>
<th>Au species</th>
<th>Cu species</th>
<th>Ce species</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Au(^{δ-}))</td>
<td>Au(^{0})</td>
<td>Au(^{δ^+})</td>
<td>Cu(^{0})</td>
</tr>
<tr>
<td>Au/CeO(_2) before</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Au/CeO(_2) after</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Au/CeZrO(_x) before</td>
<td>-</td>
<td>84</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>Au/CeZrO(_x) after</td>
<td>-</td>
<td>92</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>Au/ZrO(_2) before</td>
<td>-</td>
<td>89</td>
<td>11</td>
<td>-</td>
</tr>
<tr>
<td>Au/ZrO(_2) after</td>
<td>-</td>
<td>93</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>CuAu/CeO(_2) before</td>
<td>-</td>
<td>96</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>CuAu/CeO(_2) after</td>
<td>18</td>
<td>82</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>CuAu/CeZrO(_x) before</td>
<td>19</td>
<td>81</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CuAu/CeZrO(_x) after</td>
<td>8</td>
<td>91</td>
<td>1</td>
<td>16</td>
</tr>
<tr>
<td>CuAu/ZrO(_2) before</td>
<td>16</td>
<td>71</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>CuAu/ZrO(_2) after</td>
<td>12</td>
<td>88</td>
<td>-</td>
<td>21</td>
</tr>
</tbody>
</table>

XPS method can be used to estimate the contents of chemical elements on the external surface of solid materials. The content of gold species was determined by the chemical composition of the supports. In the case of catalysts before their using in the reaction of glycerol oxidation, the highest
Gold content on the external surface was noted in the catalysts based on pure ceria and mixed cerium-zirconium oxide (Table S1).

Gold loaded on ceria, zirconia and cerium-zirconium mixed oxide was characterised in the XP spectra by the two spin-orbit components Au 4f7/2 and Au 4f5/2 [33,62-66], separated and composed of two doublets attributed to different gold species (Figures S5 and S6), corresponding to (Au0)δ-, Au0 and/or Auδ+ species, where δ means +1 and/or +3 (Table 2). According to literature [67,68] the binding energy (BE) of Au 4f7/2 for bulk metallic gold Au0 is 83.0-84.4 eV, for Au+ – 84.5-85.0 eV and for Au3+ – 85.0-86.5 eV. It is very difficult to distinguish Au+ and Au3+ species because the presented above limits of BE ranges are not rigid and this is the reason why in this work all cationic gold species are described as Auδ+.

Table 3. The binding energy of Au 4f7/2 and Cu 2p3/2 species in the selected monometallic gold and bimetallic copper-gold catalysts before and after their using in the reaction of glycerol oxidation at 333 K for 5 h at 1200 rpm at basic conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Binding energy, eV</th>
<th>Au 4f7/2 species</th>
<th>Cu 2p3/2 species</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Au0)δ-</td>
<td>Auδ+</td>
</tr>
<tr>
<td>Au/CeO2 before</td>
<td>-</td>
<td>83.2</td>
<td>-</td>
</tr>
<tr>
<td>Au/CeO2 after</td>
<td>-</td>
<td>83.0</td>
<td>-</td>
</tr>
<tr>
<td>Au/ CeZrOx before</td>
<td>-</td>
<td>84.5</td>
<td>86.1</td>
</tr>
<tr>
<td>Au/ CeZrOx after</td>
<td>-</td>
<td>83.5</td>
<td>85.4</td>
</tr>
<tr>
<td>Au/ZrO2 before</td>
<td>-</td>
<td>83.7</td>
<td>85.5</td>
</tr>
<tr>
<td>Au/ZrO2 after</td>
<td>-</td>
<td>83.6</td>
<td>85.6</td>
</tr>
<tr>
<td>CuAu/ CeO2 before</td>
<td>-</td>
<td>83.6</td>
<td>85.4</td>
</tr>
<tr>
<td>CuAu/ CeO2 after</td>
<td>82.5</td>
<td>83.9</td>
<td>930.6</td>
</tr>
<tr>
<td>CuAu/ CeZrOx before</td>
<td>82.3</td>
<td>83.6</td>
<td>-</td>
</tr>
<tr>
<td>CuAu/ CeZrOx after</td>
<td>82.2</td>
<td>83.4</td>
<td>84.9</td>
</tr>
<tr>
<td>CuAu/ ZrO2 before</td>
<td>82.4</td>
<td>83.5</td>
<td>84.6</td>
</tr>
<tr>
<td>CuAu/ ZrO2 after</td>
<td>82.1</td>
<td>83.5</td>
<td>-</td>
</tr>
</tbody>
</table>

In the case of monometallic gold catalysts, the BE due to metallic gold (Au0) changed from 83.0 eV to 84.5 eV (Fig. S5). The lowest values of BE were observed if gold was loaded on pure ceria at 83.2 and 83.0 eV, before and after glycerol oxidation, respectively (Table 3). These values of binding energy are much lower than typical of bulk metallic gold (84.0 eV) [69]. The species characterised by BE below 83 eV were interpreted by some authors as negatively charged gold on different supports or the metallic gold particles with the partial negative charge on the external surface of metallic gold particles, e.g. [62,70,71]. The XP spectra of bimetallic copper-gold samples recorded in the range of Au 4f species were characterised by two doublets (with the exception of CuAu/ZrO2 before its using in glycerol oxidation and CuAu/ CeZrOx after glycerol oxidation), which origin depends on the nature of the supports (Fig. S6). In the case of copper-gold loaded on ceria (CuAu/ CeO2), the species were characterised by the BE of Au 4f7/2 species at 83.6 and 85.4 eV (before glycerol oxidation) and at 82.5 and 83.9 eV (after glycerol oxidation) and these values of BE can be attributed to Au0 and Auδ+ (before glycerol oxidation) and (Au0)δ- and Au0 (after glycerol oxidation), respectively. On the mixed cerium-zirconium oxide modified with gold and copper (CuAu/ CeZrOx), two bands were observed at 82.3 and 83.6 eV (before glycerol oxidation) and at 82.2, 83.4 and 84.9 eV (after glycerol oxidation), which can be due to the metallic gold particles with the partial negative charge on the external
surface of metallic gold particles \((\text{Au}^0)^\delta\) and metallic gold \((\text{Au}^0)\) (before glycerol oxidation) and to \((\text{Au}^0)^\delta, \text{Au}^0\) and \(\text{Au}^{\delta+}\) (after glycerol oxidation), respectively. \(\text{CuAu/ZrO}_2\) contained metallic and cationic gold species with the bands at 82.4, 83.5 and 84.6 eV (before glycerol oxidation) and at 82.1 and 83.5 eV (after glycerol oxidation), respectively. The lower BE observed for \(\text{Au}^0\) \(4f_{7/2}\) in the copper-gold catalysts than in monometallic gold catalysts can suggest the presence of the smaller gold particles loading on the surface of catalysts [33,66]. The smaller size of metallic gold particles in the bimetallic catalysts was confirmed by the STEM-EDXS results (Fig. S3). As concerns the appearance of XP bands in the range of ~82.1-82.9 eV, they should be attributed to the changes in electronic structure of the system and core-hole shielding.

An according to the literature data [72,73], the BE of \(\text{Cu} 2p\) species could be assigned to \(\text{Cu}^0, \text{Cu}^+\) and \(\text{Cu}^{2+}\) in the range of 930.0-932.0, 932.0-933.0 and 933.0-935.5 eV, respectively. The bimetallic copper-gold catalysts before and after their using in glycerol oxidation were the samples in which the main form of copper was reduced form – \(\text{Cu}^+\) cation (excluding \(\text{CuAu/ CeZrO}_x\) after its using in glycerol oxidation). It is interesting that in all bimetallic catalysts after their using in the glycerol oxidation, the first part of copper species \(\text{Cu}^+\) were reduced to metallic copper (\(\text{Cu}^0\)) and the second part were oxidized to cationic copper (\(\text{Cu}^{2+}\)) and the growth of zirconium content in the support led to more significant the decrease of the distribution of \(\text{Cu}^+\) species. The lower distribution of \(\text{Cu}^+\) species in the bimetallic catalysts was accompanied by the growth of the distribution of gold species as like metallic gold particles with the partial negative charge on the external surface \((\text{Au}^0)^\delta\). It can be explained by the parallel partial reduction of metallic gold \((\text{Au}^0)\) to \((\text{Au}^0)^\delta\) and the disproportion reaction of cationic copper \((\text{Cu}^+\) to metallic copper \((\text{Cu}^0)\) and cationic copper \((\text{Cu}^{2+}\) during the oxidation of glycerol in the liquid phase.

### 3. Materials and Methods

#### 3.1. Catalysts preparation

The details of catalysts preparation (monometallic gold or copper catalysts and bimetallic copper-gold catalysts) were described in earlier papers [30,32]. The nominal (assumed) molar ratio between ceria and zirconia in the catalysts based on \(\text{CeZrO}_x\) support was 1:1 (in the earlier work [30], this material was called as \(\text{CeZrO}_x(1:1)\)).

#### 3.2. Catalysts characterisation

The part of details of catalysts characterisation was described in [30,32]. In this part will be presented only the procedure of XRD, \(\text{N}_2\) adsorption and desorption isotherms, ATR-FTIR, UV-vis, XPS, TEM, SEM, STEM-EDXS study samples before and after reaction of glycerol oxidation.

##### 3.2.1. X-ray diffraction (XRD)

XRD measurements were carried out on a Bruker AXS D8 Advance diffractometer with \(\text{Cu} K\) radiation \((\lambda = 0.154 \text{ nm})\), with a step size of 0.05° in the wide angle range (21-81°). The XRD method was used to estimate the size of gold particles using the Scherrer formula before and after the reaction of glycerol oxidation at 333 K for 5 h at basic conditions.

##### 3.2.2. \(\text{N}_2\) adsorption and desorption isotherms

\(\text{N}_2\) adsorption and desorption isotherms were obtained using a Quantochrome Autosorb iQ Instruments at 77 K after pretreated around 0.200 g of powder sample \textit{in situ} under high vacuum at 573 K for 4 h. The surface area was calculated by the BET method. Mesopores volume and mean pore size were determined from BJH (adsorption branches).
3.2.3. Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR)

The ATR-FTIR measurements were recorded using a Bruker 70 Spectrometer equipped with ATR-FTIR Platinum Bruker cell to carry out the FTIR spectra for the liquid and solid samples in the range 4000-400 cm⁻¹, resolution: 4 cm⁻¹ and scans: 64.

3.2.4. Ultra-violet spectroscopy (UV-vis spectroscopy)

UV-vis spectra were recorded using a Varian-Cary 300 Scan UV-visible spectrophotometer. Powder calcined samples before and after glycerol oxidation and drying at RT for 24 h in air atmosphere were placed in a cell equipped with a quartz window. The spectra were recorded in the range from 800 to 190 nm. Spectralon® was used as the reference material.

3.2.5. XPS X-ray Photoelectron Spectroscopy (XPS)

Photoelectron spectra were recorded using an Ultra High Vacuum (UHV) System (Specs, Germany). The study was conducted using X-ray Al Kα = 1486.6 eV with the parameters of the lamp: 14.5 kV, 20 mA. Measurements were carried out in vacuum of approximately 5.0 × 10⁻⁹ mbar in the chamber of the analyser. The spectra were recorded for the energy range from 1100 eV to 0 eV in increments of 0.4 eV, the energy transition CAE = 100 eV. The XP spectra for metal species were recorded in increments of 0.1 eV, at the energy transition CAE = 30 eV and time counts 50 ms. The number of scans of the range measured was chosen to correspond to a given signal to noise ratio. The powder sample was put on the conductive tape, which was adhered to the carrier surface and positioned in perpendicular to the axis of the analyser. The X-ray source was set at an angle of 60° to the plane of the surface. The area of the samples analysed corresponded to the size of the aperture of the analyser used (large area), ca. 50 mm². Deconvolution of XP spectra was carried out using OMNIC 8.0™ software. Band intensities were estimated by calculating the integral of each band after smoothing and baseline correction, then set the deconvolution parameters for the experimental curve using the software – Gaussian function, signal sensitivity: small and base line: linear. Atomic ratios were computed from the intensity ratios normalized by atomic sensitivity factors. An estimated error of ±0.1 eV can be assumed for all measurements.

3.2.6. Transmission electron microscopy (TEM)

The powders were deposited on a grid covered with a holey carbon film and transferred to JEOL 2000 electron microscope operating at 80 kV. Before measurement, samples were made in the form of a suspension in 1-butanol. The size of particles was estimated using ImageJ™ software.

3.2.7. Scanning electron microscopy (SEM)

The samples in the form of powders were deposited on a grid covered with a holey carbon film and transferred to Philips SEM 515 scanning electron microscope. Before measurement, samples were made in the form of a suspension in 1-butanol.

3.2.8. Scanning transmission electron microscopy- energy dispersive X-ray (STEM-EDXS)

Metal particles of gold were characterised using scanning transmission electron microscopy (STEM) and estimated using ImageJ™ software. STEM images were acquired with an aberration-corrected dedicated STEM microscope HD 2700 CS (Hitachi, acceleration potential of 200 kV) and obtained with a high-angle annular dark-field (HAADF) detector to produce images with atomic number (Z) contrast.

3.3. Catalytic test – reaction of glycerol oxidation

The process of glycerol oxidation was performed in a Berghof-25 (Germany) autoclave reactor (25 cm³) using a catalyst suspension in 15.00 g (in the pressure of O₂, 5.0 N, Linde) or 14.25 g (in the...
presence of H₂O₂, 30 %, Fluke) of distilled water with 1.5 mmol of glycerol (138 mg, >99.0 %, Sigma-Aldrich) and 1.5 or 3.0 mmol of NaOH (60 or 120 mg, >99.0%, Merck) or 0.028 mmol of HNO₃ (2.7 mg, 65 %, Sigma-Aldrich). The reaction was conducted at 333 K at 400, 800, 1000 or 1200 rpm in the pressure of oxygen (3 or 6 bars) or in the presence of hydrogen peroxide (0.75 g, 30 %, Sigma-Aldrich). The liquid products and un-reacted glycerol were determined quantitatively by a HPLC system equipped in RI and UV-vis detectors. More details of the analysis using a HPLC device were reported in [30].

4. Conclusions

The results of the selective oxidation of glycerol over the mesoporous ceria, zirconia or cerium-zirconium oxide with Cu and/or Au show that the Cu-Au catalysts can be attractive catalysts for the oxidation of organic compounds in the liquid phase at selected conditions. The increase of zirconium content in the support has a positive effect on the catalytic stability and the growth of selectivity to the main product – glyceric acid, because the highest selectivity (93 %) was achieved at basic condition at 333 K over CuAu/ZrO₂ after the 2nd cycle of oxidation (at 1200 rpm). The obtained results provided the earlier results that the bimetallic copper-gold catalysts are more active in oxidation process in the gas phase than analogues monometallic gold catalysts [74,75]. The metallic gold on the surface of catalysts modified with copper species can lead to the appearance of the electron interaction between both metals. This interaction can facilitate the reduction of copper species – Cu⁺ and Cu²⁺ cations (the presence of these species was provided by the UV-vis and XPS) and the higher mobility of oxygen-promoting oxidative properties confirmed by XPS study. Copper has a larger electron-donating ability and it can modify the electronic properties of metallic gold. The achieved results of glycerol oxidation show that many parameters determine the effectiveness of glycerol oxidation, e.g. the chemical composition of support, the texture and structure properties, and also conditions of reaction (source of oxygen, pH, concentration of base and oxygen, temperature and speed stirring).

Supplementary Materials: The following are available online at www.mdpi.com/ link, Figure S1: XRD patterns of catalysts based on: A) CeO₂; B) CeZrOₓ and C) ZrO₂, before (a) and after (b) their using as catalysts in the reaction of glycerol oxidation at basic conditions at 333 K for 5 h at 1000 rpm. The reflections were marked using symbols: ● means the crystal phase of ceria in cubic coordination, ○ and □ are the crystal phases of zirconia in tetrahedral and monoclinic coordination, respectively, ■ is due to the crystal phase of metallic gold particles, Figure S2: Isotherms of adsorption and desorption of nitrogen at 77 K performed for the catalysts: A) CeO₂; B) Au/CeO₂; C) CuAu/CeO₂; D) ZrO₂; E) Au/ZrO₂ and F) CuAu/ZrO₂, before their using as catalysts in the reaction of glycerol oxidation, Figure S3: The SEM (left side) and TEM (right side) images performed for CuAu/ZrO₂ before its using in glycerol oxidation, Figure S4: STEM images and EDX spectra recorded for CuAu/CeZrOₓ before and after its using as catalyst in glycerol oxidation at 333 K for 5 h at 1000 rpm at basic conditions, Figure S5: XPS spectra of 4f Au species region recorded for the catalysts: A) Au/CeO₂; B) Au/CeZrOₓ and C) Au/ZrO₂ before and after their performance as catalysts in the reaction of glycerol oxidation, Figure S6: XPS spectra of 4f Au species region recorded for the catalysts: A) CuAu/CeO₂; B) CuAu/CeZrOₓ and C) CuAu/ZrO₂ before and after their performance as catalysts in the reaction of glycerol oxidation.

Acknowledgments: The author would like to acknowledge for the financial support the National Science Centre in Cracow in Poland (project No. 2015/16/T/ST5/00263) and the Scientific Exchange Programme Sciex-NMSch (application No. 12.258). The author thanks ETH in Zurich (Switzerland) for the sharing of STEM-EDXS and HPLC equipment. P. Kaminski would like to thank Prof. Maria Ziolek (Adam Mickiewicz University in Poznan, the Faculty of Chemistry) and Prof. Jeroen A. van Bokhoven (ETH Zurich) for a fruitful discussion and value remarks.

Author Contributions: P.K. conceived, designed and performed all experiments, analysed all data, contributed reagents/materials/analysis tools and wrote the paper.
Conflicts of Interest: The author declares no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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