Electronic Supporting Information

Mesoporous cerium-zirconium oxides modified with gold and copper – synthesis, characterization and performance in selective oxidation of glycerol

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Figure S1. The nitrogen adsorption/desorption isotherms for selected catalysts.
Figure S2. STEM images and EDX spectra of CuAu/CeZrO$_x$(1:1).
Figure S3. XP spectra of Au 4f region recorded for selected catalysts.
Figure S4. Oxygen consumption (left side) and correlation between molar ratio O₂/glycerol in reaction mixture (right side) during the reaction of glycerol oxidation at 333 K for 5 h at 1000 rpm for the Cu-Au catalysts, where: ● – CuAu/CeO₂; ♦ – CuAu/CeZrOₓ(2:1); ▲ – CuAu/CeZrOₓ(1:1); □ – CuAu/CeZrOₓ(1:2) and ■ – CuAu/ZrO₂.
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<th>temp., K</th>
<th>rpm</th>
<th>conv., %</th>
<th>selectivity, %</th>
<th>1,3-DHA&lt;sup&gt;i&lt;/sup&gt;</th>
<th>gaseous products&lt;sup&gt;i&lt;/sup&gt;</th>
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<sup>a</sup> OA – oxalic acid
<sup>b</sup> TA – tartronic acid
<sup>c</sup> GLO – glyoxylic acid
<sup>d</sup> GLA – glyceric acid
<sup>e</sup> LA – lactic acid
<sup>f</sup> GCA – glycolic acid
<sup>g</sup> FA – formic acid
<sup>h</sup> 1,3-DHA – 1,3-dihydroxyacetone
<sup>i</sup> gaseous products – CO<sub>2</sub> and other gases
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a OA – oxalic acid
b TA – tartronic acid
c GLO – glyoxylic acid
d GLA – glyceric acid
e LA – lactic acid
f GCA – glycolic acid
g FA – formic acid
h 1,3-DHA – 1,3-dihydroxyacetone
i gaseous products – CO₂ and other gases
**Table S3.** Comparison of TOF in glycerol oxidation over selected catalysts.

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<th>catalyst</th>
<th>Au content, % wt. (^a)</th>
<th>size of Au particle, nm (^b)</th>
<th>GLY conv., % (^c)</th>
<th>GLA selectivity, % (^c)</th>
<th>reaction conditions</th>
<th>TOF, h(^{-1})</th>
<th>reference</th>
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<td>3.6</td>
<td>33 (^c)</td>
<td>78 (^c)</td>
<td>0.138 g of glycerol,</td>
<td>667 (^d)</td>
<td>this paper</td>
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<td>n.d.</td>
<td>43 (^c)</td>
<td>74 (^c)</td>
<td>NaOH:glycerol = 2:1,</td>
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<td>2.2</td>
<td>33 (^c)</td>
<td>89 (^c)</td>
<td>6 bar O(_2), 333 K,</td>
<td>618 (^d)</td>
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<td>glycerol/metal – 1000/1 (mol/mol), 15 ml of solution</td>
<td>901 (^d)</td>
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<td>1.6</td>
<td>39 (^c)</td>
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<td>1236 (^d)</td>
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<td>2.2</td>
<td>50</td>
<td>56</td>
<td>glycerol 0.3 M, NaOH/glycerol = 4, 3 atm O(_2), 323 K, glycerol/metal – 1000/1 (mol/mol), 10 ml of solution</td>
<td>1390 (^e)</td>
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<td>113 (^f)</td>
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<td>Au/AC (activated carbon)</td>
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<td>52</td>
<td>1090 (^d)</td>
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<td>90</td>
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<td>1418 (^f)</td>
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<td>Au(_{PVA(1:0.125)})/TiO(_2)</td>
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<td>4.1</td>
<td>90</td>
<td>70</td>
<td>glycerol 0.3 M, 4 eq NaOH, 300 kPa O(_2), 323 K, glycerol/metal – 1000/1 (mol/mol), 10 ml of solution</td>
<td>434 (^f)</td>
<td>90</td>
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GLY – glycerol, GLA – glycolic acid

\(^a\) from TEM images

\(^b\) from ICP analysis

\(^c\) after 30 min of glycerol oxidation

\(^d\) TOF was calculated on the base of total Au loading (from ICP) after 30 min of the reaction as the moles of glycerol converted per one hour per one mol of metal (gold)

\(^e\) TOF was calculated on the base of total Au loading (from ICP) after 60 min of the reaction as the moles of glycerol converted per one hour per one mol of metal (gold)

\(^f\) TOF was calculated on the base of total Au loading (from ICP) after 15 min of the reaction as the moles of glycerol converted per one hour per one mol of metal (gold)
The results of glycerol oxidation over bimetallic Cu-Au catalysts at 363 K.

<table>
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<th>catalyst</th>
<th>rpm</th>
<th>conv., %</th>
<th>selectivity, %</th>
<th>1,3-DHA</th>
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<td>CuAu/CeO₂</td>
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<tr>
<td>CuAu/CeZrOₓ(2:1)</td>
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<td>CuAu/CeZrOₓ(1:1)</td>
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<td>66</td>
<td>4</td>
<td>64</td>
<td>-</td>
</tr>
<tr>
<td>CuAu/CeZrOₓ(1:2)</td>
<td></td>
<td>87</td>
<td>-</td>
<td>78</td>
<td>7</td>
</tr>
<tr>
<td>CuAu/CeO₂</td>
<td></td>
<td>72</td>
<td>1</td>
<td>67</td>
<td>traces</td>
</tr>
<tr>
<td>CuAu/CeZrOₓ(2:1)</td>
<td></td>
<td>74</td>
<td>2</td>
<td>61</td>
<td>27</td>
</tr>
<tr>
<td>CuAu/CeZrOₓ(1:1)</td>
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<td>97</td>
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<td>63</td>
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<tr>
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<td></td>
<td>93</td>
<td>2</td>
<td>61</td>
<td>26</td>
</tr>
<tr>
<td>CuAu/ZrO₂</td>
<td></td>
<td>94</td>
<td>traces</td>
<td>61</td>
<td>28</td>
</tr>
</tbody>
</table>

* OA – oxalic acid
* TA – tartronic acid
* GLO – glyoxylic acid
* GLA – glyceric acid
* LA – lactic acid
* GCA – glycolic acid
* FA – formic acid
* 1,3-DHA – 1,3-dihydroxyacetone
* gaseous products – CO₂ and other gases
Table S5. The comparison of metal contents before (for fresh samples) and after the second cycle (after recycling) measured using the ICP-OES method.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>metal species content, wt %</th>
<th></th>
<th></th>
<th></th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Au (fresh sample)</td>
<td>Au (after recycling)</td>
<td>Cu (fresh sample)</td>
<td>Cu (after recycling)</td>
</tr>
<tr>
<td>CuAu/CeO₂</td>
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<td>0.8</td>
<td>1.7</td>
<td>0.8</td>
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<tr>
<td>CuAu/CeZrOₓ(2:1)</td>
<td>1.0</td>
<td>0.6</td>
<td>1.6</td>
<td>1.0</td>
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<tr>
<td>CuAu/CeZrOₓ(1:1)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.7</td>
<td>0.9</td>
</tr>
<tr>
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<td>0.8</td>
<td>1.7</td>
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<tr>
<td>CuAu/ZrO₂</td>
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<td>0.4</td>
<td>1.8</td>
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