Electronic Supporting Information

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

Piotr Kaminski[a,b*], Maria Ziolek[a*], Jeroen A. van Bokhoven[b,c*]

[a]Adam Mickiewicz University in Poznań, Faculty of Chemistry, ul. Umultowska 89b, 61-614 Poznań, Poland

[b]ETH Zürich, Institute for Chemical and Bioengineering, Vladimir-Prelog-Weg 1, CH-8093 Zürich, Switzerland

[c]Paul Scherrer Institute, Laboratory for Catalysis and Sustainable Chemistry, CH-5232 Villigen, Switzerland

**piotr.kaminski@amu.edu.pl*

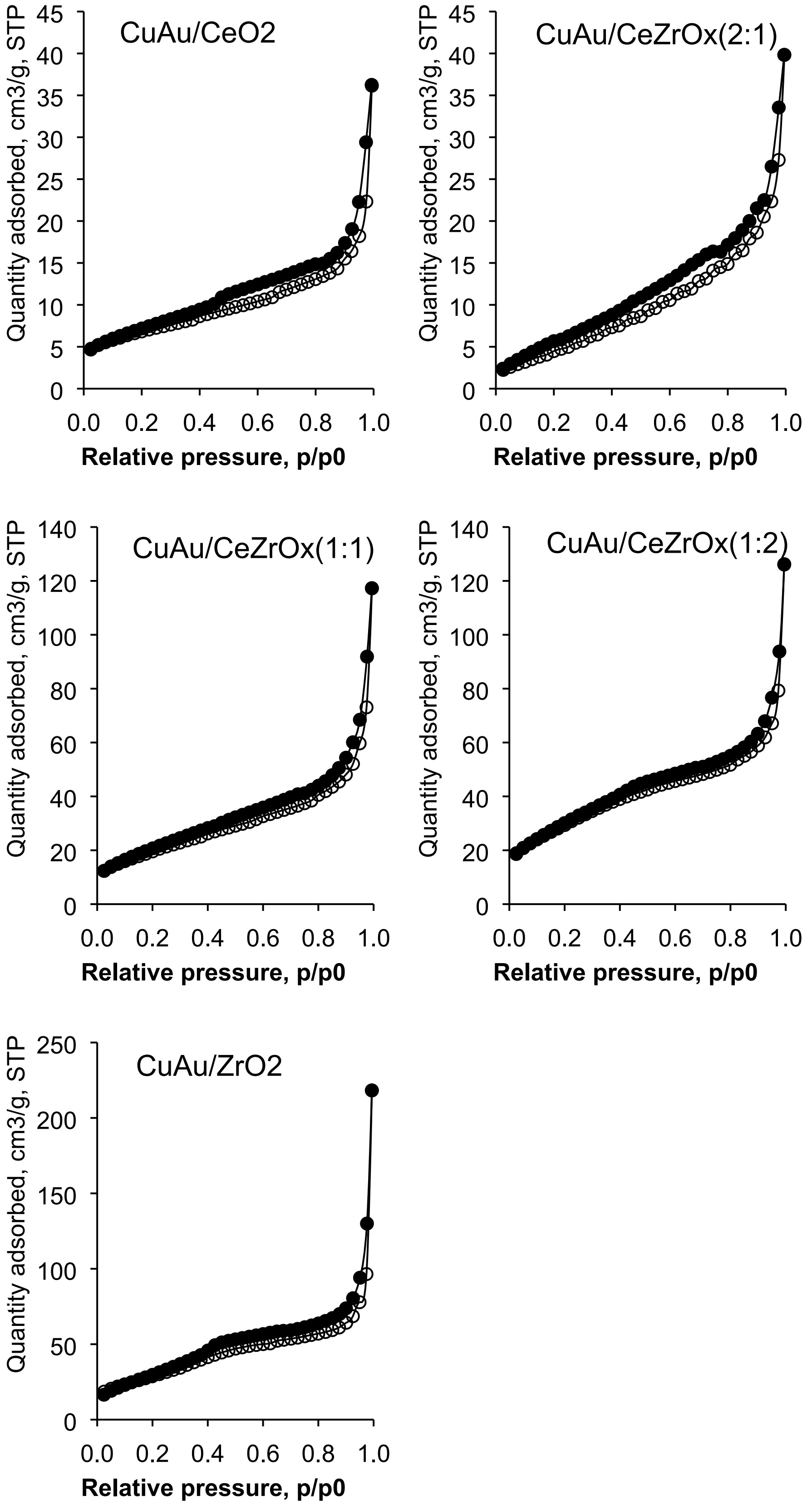

Figure S1. The nitrogen adsorption/desorption isotherms for selected catalysts.

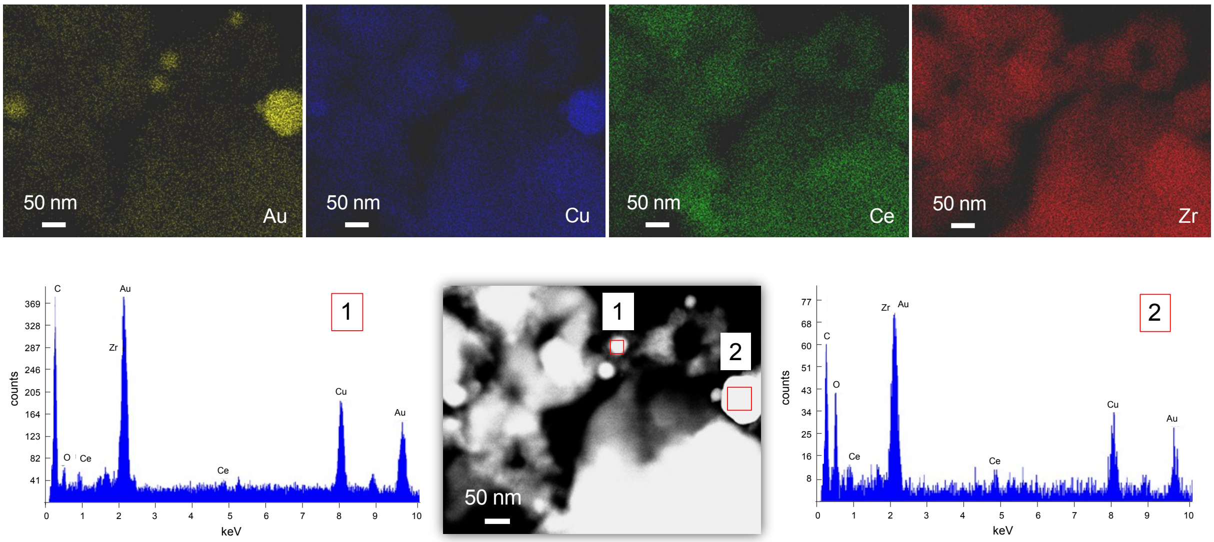

Figure S2. STEM images and EDX spectra of $CuAu/CeZrO_x$(1:1).

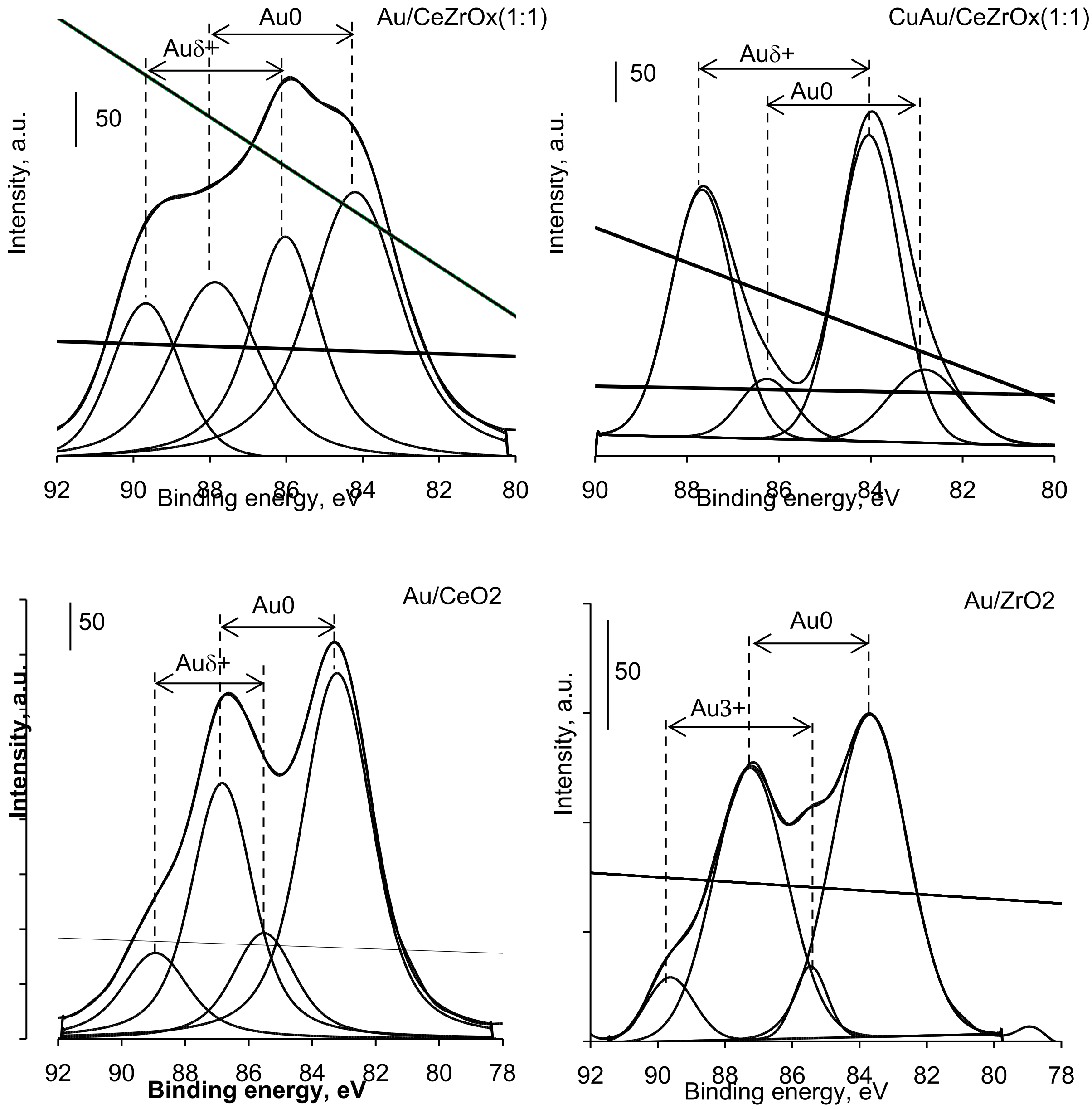

Figure S3. XP spectra of Au 4f region recorded for selected catalysts.

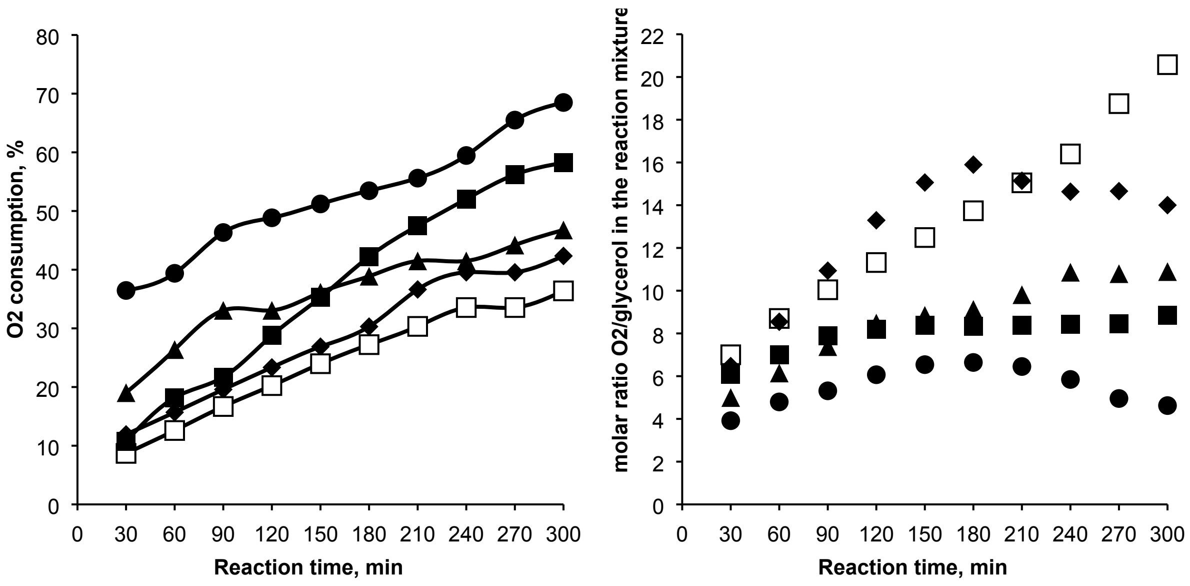

Figure S4. Oxygen consumption (left side) and correlation between molar ratio O_2/glycerol in reaction mixture (right side) during the reaction of glycerol oxidation at 333 K for 5 h at 1000 rpm for the Cu-Au catalysts, where: ● – CuAu/CeO_2; ♦ – CuAu/$CeZrO_x$(2:1); ▲ – CuAu/$CeZrO_x$(1:1); □ – CuAu/$CeZrO_x$(1:2) and ■ – CuAu/ZrO_2.

Table. S1. The results of glycerol oxidation over monometallic Au catalysts.

catalyst	temp., K	rpm	conv., %	selectivity, %								
				OA[a]	TA[b]	GOA[c]	GLA[d]	LA[e]	GCA[f]	FA[g]	1,3-DHA[h]	gaseous products[i]
Au/CeO_2			24	-	traces	-	9	-	traces	-	-	91
Au/$CeZrO_x$(2:1)			9	-	traces	-	16	-	1	-	traces	83
Au/$CeZrO_x$(1:1)	333	400	16	-	traces	-	1	traces	traces	-	-	99
Au/$CeZrO_x$(1:2)			14	-	traces	-	1	traces	-	-	-	99
Au/ZrO_2			7	-	traces	-	2	traces	-	-	-	98
Au/CeO_2			95	1	3	-	49	39	-	7	1	-
Au/$CeZrO_x$(2:1)			78	1	2	-	69	-	13	15	-	-
Au/$CeZrO_x$(1:1)	363	400	69	1	3	-	66	-	12	18	-	traces
Au/$CeZrO_x$(1:2)			45	-	2	-	34	2	-	2	traces	60
Au/ZrO_2			28	traces	traces	-	26	-	1	3	-	70
Au/CeO_2			17	traces	1	-	26	-	1	1	-	71
Au/$CeZrO_x$(2:1)			20	-	traces	-	12	-	traces	-	-	88
Au/$CeZrO_x$(1:1)	333	800	10	-	traces	-	9	-	-	-	-	91
Au/$CeZrO_x$(1:2)			4	-	traces	-	9	-	traces	-	-	91
Au/ZrO_2			11	-	traces	traces	2	traces	-	-	-	98
Au/CeO_2			83	2	2	-	65	22	-	9	traces	-
Au/$CeZrO_x$(2:1)			60	2	1	-	52	13	-	8	-	24
Au/$CeZrO_x$(1:1)	363	800	62	traces	1	-	69	10	-	5	1	14
Au/$CeZrO_x$(1:2)			49	1	1	-	49	3	-	5	-	41
Au/ZrO_2			48	-	1	-	48	3	-	2	-	46
Au/CeO_2			40	-	traces	-	19	1	-	1	-	79
Au/$CeZrO_x$(2:1)			35	-	traces	-	10	traces	-	traces	-	90
Au/$CeZrO_x$(1:1)	333	1000	35	-	traces	-	6	-	-	-	-	94
Au/$CeZrO_x$(1:2)			15	-	traces	-	7	-	-	-	-	93
Au/ZrO_2			30	-	traces	-	5	-	-	-	-	95
Au/CeO_2			31	-	traces	-	18	1	-	1	-	80
Au/$CeZrO_x$(2:1)			30	-	traces	-	10	traces	-	traces	-	90
Au/$CeZrO_x$(1:1)	333	1200	32	-	traces	-	18	1	-	1	-	80
Au/$CeZrO_x$(1:2)			19	-	traces	-	7	-	-	traces	-	93
Au/ZrO_2			19	-	traces	-	4	-	-	-	-	96

[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-dihydroxyacetonei
[i] gaseous products – CO_2 and other gases

Table. S2. The results of glycerol oxidation over monometallic Cu catalysts.

catalyst	temp., K	rpm	conv., %	selectivity, %								
				OA[a]	TA[b]	GOA[c]	GLA[d]	LA[e]	GCA[f]	FA[g]	1,3-DHA[h]	gaseous products[i]
Cu/CeO_2	333	400	19	-	traces	-	7	-	2	1	-	90
$Cu/CeZrO_x$(2:1)			16	-	traces	-	6	-	1	traces	-	93
$Cu/CeZrO_x$(1:1)			24	-	traces	-	1	traces	1	-	-	98
$Cu/CeZrO_x$(1:2)			11	-	traces	-	1	1	traces	-	-	98
Cu/ZrO_2			8	-	traces	-	1	traces	1	-	-	98
Cu/CeO_2	363	400	39	traces	1	-	24	-	18	23	traces	34
$Cu/CeZrO_x$(2:1)			29	-	1	traces	16	-	11	11	-	61
$Cu/CeZrO_x$(1:1)			52	traces	1	-	33	-	14	18	-	34
$Cu/CeZrO_x$(1:2)			45	1	2	traces	32	-	14	19	-	32
Cu/ZrO_2			35	-	1	-	22	-	9	10	-	58
Cu/CeO_2	333	800	11	-	traces	-	1	traces	1	1	-	97
$Cu/CeZrO_x$(2:1)			25	-	traces	-	1	traces	traces	-	-	99
$Cu/CeZrO_x$(1:1)			23	-	traces	-	2	traces	1	-	-	97
$Cu/CeZrO_x$(1:2)			3	-	traces	-	2	traces	1	-	-	97
Cu/ZrO_2			11	-	traces	-	1	1	traces	-	-	98
Cu/CeO_2	363	800	53	1	1	-	40	-	23	33	-	2
$Cu/CeZrO_x$(2:1)			56	traces	2	-	40	-	18	24	-	16
$Cu/CeZrO_x$(1:1)			45	traces	1	-	32	-	16	22	-	29
$Cu/CeZrO_x$(1:2)			42	1	1	-	43	-	16	22	-	17
Cu/ZrO_2			35	-	2	-	39	-	13	15	-	31
Cu/CeO_2	333	1000	19	-	traces	-	7	-	2	1	-	90
$Cu/CeZrO_x$(2:1)			31	-	-	-	9	-	2	1	-	88
$Cu/CeZrO_x$(1:1)			35	-	traces	-	5	-	1	traces	-	94
$Cu/CeZrO_x$(1:2)			28	-	traces	-	7	-	1	1	-	91
Cu/ZrO_2			28	-	traces	-	7	-	2	1	-	90
Cu/CeO_2	333	1200	27	-	traces	-	7	-	2	traces	-	91
$Cu/CeZrO_x$(2:1)			29	-	traces	-	11	-	3	2	-	84
$Cu/CeZrO_x$(1:1)			20	-	traces	-	6	-	1	traces	-	93
$Cu/CeZrO_x$(1:2)			30	-	traces	-	6	-	1	1	-	92
Cu/ZrO_2			26	-	traces	-	7	-	2	1	-	90

[a] OA – oxalic acid
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[d] GLA – glyceric acid
[e] LA – lactic acid
[f] GCA – glycolic acid
[g] FA – formic acid
[h] 1,3-DHA – 1,3-dihydroxyacetonei
[i] gaseous products – CO_2 and other gases

Table S3. Comparison of TOF in glycerol oxidation over selected catalysts.

catalyst	Au content, % wt. [a]	size of Au particle, nm [b]	GLY conv., %	GLA selectivity, %	reaction conditions	TOF, h^{-1}	reference
CuAu/CeO_2	1.0	3.6	33 [c]	78 [c]	0.138 g of glycerol, NaOH:glycerol = 2:1, 6 bar O_2, 333 K, glycerol/metal – 1000/1 (mol/mol), 15 ml of solution	667 [d]	this paper
CuAu/$CeZrO_x$(2:1)	1.0	n.d.	43 [c]	74 [c]		838 [d]	
CuAu/$CeZrO_x$(1:1)	1.0	2.2	33 [c]	89 [c]		618 [d]	
CuAu/$CeZrO_x$(1:2)	1.0	n.d.	46 [c]	78 [c]		901 [d]	
CuAu/ZrO_2	0.6	1.6	39 [c]	80 [c]		1236 [d]	
Au$MgAl_2O_4$ (DP calcined, CP)	1.5	2.2	50	56	glycerol 0.3 M, NaOH/glycerol = 4, 3 atm O_2, 323 K, glycerol/metal – 1000/1 (mol/mol), 10 ml of solution	1390 [e]	[28]
Au/TiO_2 (DP, calcined)	1	5	50	81	glycerol 0.3 M, NaOH/glycerol = 4, 3 atm O_2, 323 K, glycerol/metal – 500/1 (mol/mol), 10 ml of solution	113 [d]	[62]
Au/AC (activated carbon)	1.5	5	50	52		1090 [d]	
Au/NiO	1	3.6	90	55	glycerol 0.3 M, 4 eq NaOH, 300 kPa O_2, 323 K, glycerol/metal – 1000/1 (mol/mol), 10 ml of solution	1418 [f]	[89]
Au $_{PVA(1:0.125)}$/TiO_2	1	4.1	90	70	glycerol 0.3 M, 4 eq NaOH, 300 kPa O_2, 323 K, glycerol/metal – 1000/1 (mol/mol), 10 ml of solution	434 [f]	[90]

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)

Table S4. The results of glycerol oxidation over bimetallic Cu-Au catalysts at 363 K.

catalyst	rpm	conv., %	selectivity, %								
			OA[a]	TA[b]	GOA[c]	GLA[d]	LA[e]	GCA[f]	FA[g]	1,3-DHA[h]	gaseous products[i]
CuAu/CeO_2	400	65	1	1	-	52	-	14	20	-	13
CuAu/$CeZrO_x$(2:1)		61	2	1	-	42	19	-	7	traces	29
CuAu/$CeZrO_x$(1:1)		89	-	2	-	68	21	-	8	1	-
CuAu/$CeZrO_x$(1:2)		66	-	4	-	64	-	10	15	-	6
CuAu/ZrO_2		87	-	2	-	78	7	1	10	-	-
CuAu/CeO_2	800	72	1	1	-	67	traces	9	22	traces	-
CuAu/$CeZrO_x$(2:1)		74	2	1	2	61	27	-	7	1	-
CuAu/$CeZrO_x$(1:1)		97	1	2	-	63	25	-	8	1	-
CuAu/$CeZrO_x$(1:2)		93	2	2	1	61	26	-	9	1	-
CuAu/ZrO_2		94	traces	3	1	61	28	-	6	1	-

[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-dihydroxyacetonei
[i] gaseous products – CO_2 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.

catalyst	metal species content, wt %			
	Au (fresh sample)	Au (after recycling)	Cu (fresh sample)	Cu (after recycling)
CuAu/CeO_2	1.0	0.8	1.7	0.8
CuAu/$CeZrO_x$(2:1)	1.0	0.6	1.6	1.0
CuAu/$CeZrO_x$(1:1)	1.0	1.0	1.7	0.9
CuAu/$CeZrO_x$(1:2)	1.0	0.8	1.7	1.7
CuAu/ZrO_2	0.6	0.4	1.8	1.6