Electronic Supplementary Material (ESI) for Catalysis Science & Technology.


# Effect of ultra-low amount of gold in oxide-supported bimetallic Au-Fe and Au-Cu catalysts on liquid-phase aerobic glycerol oxidation in water

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## XRD data

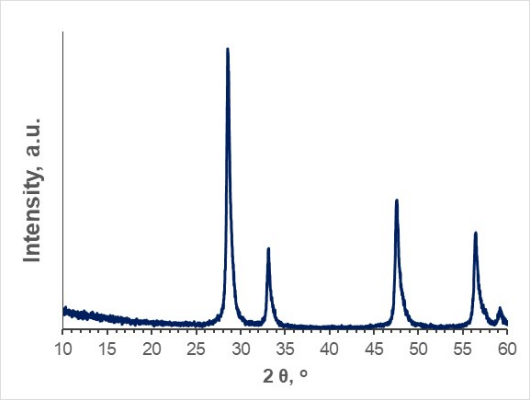


**Fig. S1**. XRD pattern of $CeO_2$

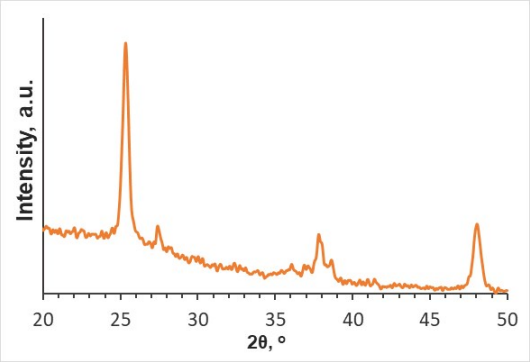


**Fig. S2**. XRD pattern of $TiO_2$-P25

### DRIFTS-CO of $CeO_2$-supported monometallic catalysts

The DPU method used for the preparation of monometallic catalysts allowed us to obtain $Cu^+$ and $Cu^{2+}$ cations on the surface of $TiO_2$ and $CeO_2$ without calcination. In the DRIFTS spectrum of CO adsorbed on the non-calcined $1Cu/CeO_2$ sample, there is a band at 2099 $cm^{-1}$, which gradually disappears after evacuation at 20-90°C without any noticeable band shift (Fig. 1 A). This band was attributed to the linear carbonyl $Cu^+$-CO formed either due to $Cu^{2+}$ reduction to $Cu^+$ with CO or CO interaction with surface cations $Cu^+$ [1,2]. Calcination of the $1Cu/CeO_2$ sample at 400°C caused the band shift to 2117 $cm^{-1}$, which could be explained by the formation of copper oxide species with larger sizes and/or new copper sites with a lower electron density.

For the non-calcined $1Fe/CeO_2$, there are two intense bands at 2188 and 1992 $cm^{-1}$ in the DRIFTS-CO spectrum after evacuation at 300°C, which can be attributed to fragments of complexes formed by interaction of Fe species and products of urea decomposition (Fig. 2 A). In the spectrum of the calcined sample, these two bands disappeared (Fig. 2 B). In the region 2500-1800 $cm^{-1}$, a band at 2170 $cm^{-1}$ can be reliably assigned to $Fe^{2+}$-CO (Fig. 3 A).

1 K. I. Hadjiivanov and G. N. Vayssilov, in *Advances in Catalysis*, Elsevier, 2002, vol. 47, pp. 307–511.
2 K. Hadjiivanov, D. Klissurski, M. Kantcheva and A. Davydov, *Faraday Trans.*, 1991, **87**, 907.

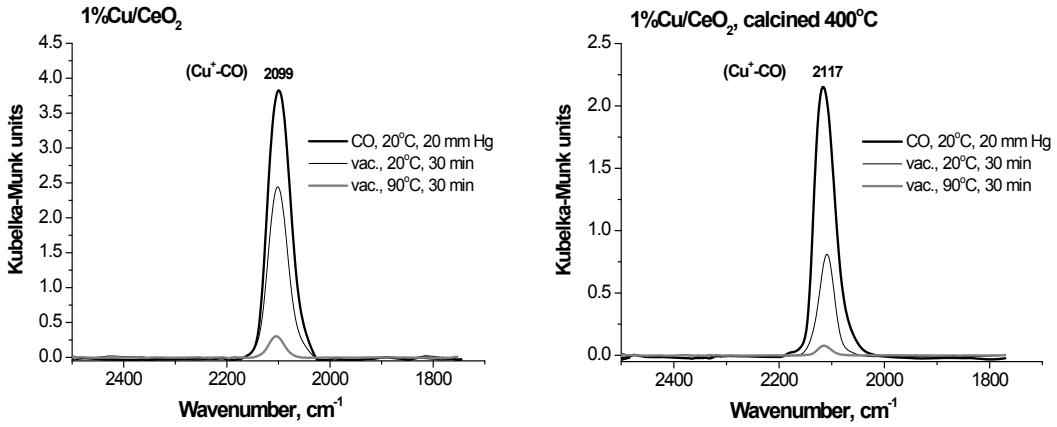


**Fig. S3.** DRIFTS-CO spectra for $1Cu/CeO_2$ before (A) and after calcination at 400°C (B).

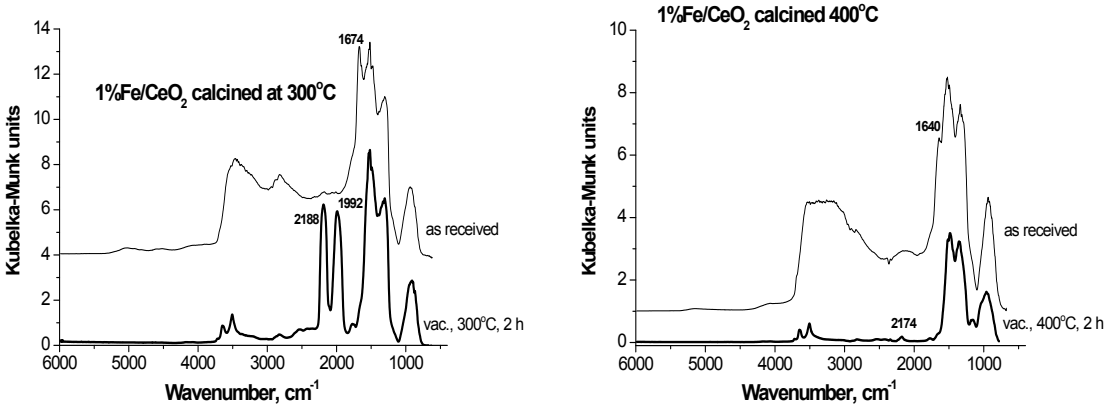


**Fig. S4.** DRIFTS-CO spectra for $1Fe/CeO_2$ before (1) and after calcination at 400°C (2).

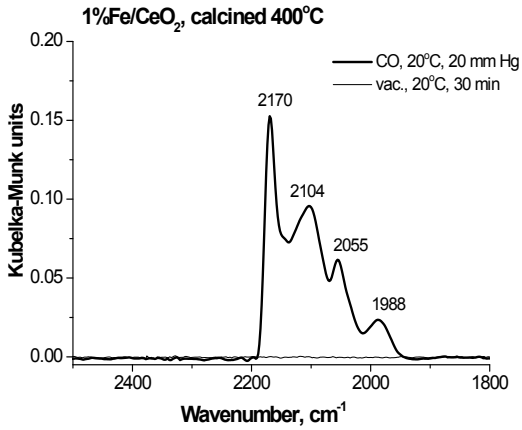


**Fig. S5.** DRIFTS-CO spectra for $1Fe/CeO_2$ after calcination at 400°C.

## XPS results

**Table S1.** XPS data and share of each peak component for supported Au-$FeO_x$ catalysts

| Sample | BE | O1s | | Au4f | | $Ti2p_{3/2}$ | $Fe2p_{3/2}$ | | Ce3d U"' |
|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 1 | 2 | | $Fe^{2+}$ | $Fe^{3+}$ | |
| 0.5Au/1Fe/$TiO_2$ | E, eV | 529.9 | 531.4 | 83.6 | 84.2 | 458.8 | 708.7 | 710.3 | |
| | % | 85 | 15 | 90 | 10 | 100 | 40 | 60 | |
| 0.1%Au/1Fe/$TiO_2$ | E, eV | 529.9 | 531.3 | 83.7 | 84.8 | 458.7 | 708.9 | 710.3 | |
| | % | 86 | 14 | 83 | 17 | 100 | 40 | 60 | |
| 0.1Au/1Fe/$CeO_2$ | E, eV | 529.4 | 531.0/ 532.0 | 83.8 | | | - | - | 916.7 |
| | % | 70 | 10/20 | - | | | | | |
| 0.025Au/1Fe/$TiO_2$ | E, eV | 529.9 | 531.2 | 83.5 | 84.6 | 458.7 | 708.7 | 710.4 | |
| | % | 86 | 14 | 80 | 20 | 100 | 55 | 45 | |
| 0.025Au/1Fe/$TiO_2$-$O_2$ | E, eV | 529.9 | 531.2 | 83.5 | 84.5 | 458.7 | 708.7 | 710.5 | |
| | % | 86 | 14 | 76 | 24 | 100 | 40 | 60 | |

**Table S2**. Theoretically calculated and experimentally obtained by XPS atomic concentration of elements

| | Experimental, % at. | | | | | Nominal, % at. | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample | O | Ti2p | Fe | Au | Ce | Ti2p | Fe | Au | Ce |
| 0.5Au/1FeO/$TiO_2$ | 71.3 | 26.7 | 1.7 | 0.24 | - | 33 | 1.4 | 0.19 | - |
| 0.1Au/1Fe/$TiO_2$ | 71.1 | 26.9 | 1.9 | 0.12 | - | 33 | 1.4 | 0.04 | - |
| 0.1Au/1Fe/$CeO_2$ | 62.4 | - | - | 0.02 | 28.4 | - | - | 0.086 | 33 |
| 0.025Au/1Fe/$TiO_2$ | 70.5 | 28.2 | 1.3 | 0.02 | - | 33 | 1.4 | 0.01 | - |
| 0.025Au/1Fe/$TiO_2$-$O_2$ | 70.4 | 28.1 | 1.4 | 0.04 | - | 33 | 1.4 | 0.01 | - |

**Table S3**. Theoretically calculated and experimentally obtained by XPS atomic ratios of elements

| | Experimental | | | | Nominal | | | |
|---|---|---|---|---|---|---|---|---|
| Sample | Ti/Fe | Ti/Au | Ce/Au | Ce/Fe | Ti/Fe | Ti/Au | Ce/Au | Ce/Fe |
| 0.5Au/1Fe/$TiO_2$ | 15.7 | 111 | - | - | 23.6 | 174 | - | - |
| 0.1Au/1Fe/$TiO_2$ | 14.2 | 224 | - | - | 23.6 | 825 | - | - |
| 0.1Au/1Fe/$CeO_2$ | - | - | 1795 | - | - | - | 384 | - |
| 0.025Au/1Fe/$TiO_2$ | 21.7 | 1410 | - | - | 23.6 | 3300 | - | - |
| 0.025Au/1Fe/$TiO_2$-$O_2$ | 20.1 | 703 | - | - | 23.6 | 3300 | - | - |

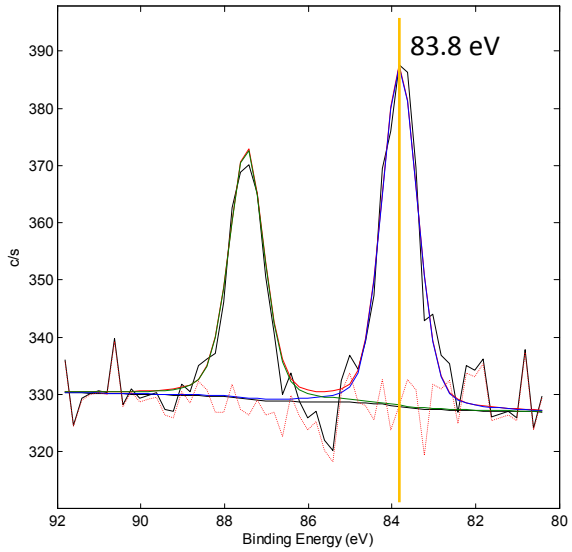


**Fig. S6.** HR XP-spectrum of Au 4F for 0.1%Au/1%$FeO_x$/$CeO_2$.

## TPR-$H_2$ data

**Table. S4**. TPR-$H_2$ data for 1%$CuO_x$/$CeO_2$ and 0.1%Au/1%$CuO_x$/$CeO_2$ catalysts

| Sample | T, °C | T max, °C | $H_2$/Cu, mol/mol |
|---|---|---|---|
| **1Cu/$CeO_2$** | 20-158 | 155 | 0.98 |
| | 158-254 | 191 | 6.04 |
| **0.1Au/1Cu/$CeO_2$** | 20-170 | 153 | 0.48 |
| | 170-254 | 187 | 0.34 |

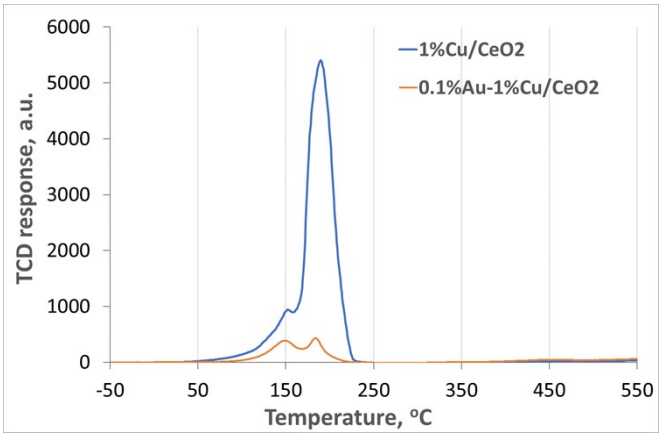


**Fig. S7**. TPR-$H_2$ curves for 1Cu/$CeO_2$ and 0.1Au/1Cu/$CeO_2$ catalysts

**Table S5**. TPR-$H_2$ data for 1%$FeO_x$/$CeO_2$ and Au/$FeO_x$/$CeO_2$ catalysts

| Sample | T, °C | T max, °C | $H_2$ µmol/g | $H_2$/Fe, mol/mol | $H_2$ theor µmol/g |
|---|---|---|---|---|---|
| **1Fe/$CeO_2$** | 20-450 | 349 | 227 | 1.27 | 59 |
| | 450-650 | 592 | 160 | 0.89 | |
| | 650-850 | - | 640 | 3.57 | |
| **0.1Au/1Fe/$CeO_2$** | 20-377 | 349 | 125 | 0.70 | 15.2 |
| | 377-431 | 382 | 37 | 0.21 | |
| | 431-500 | 464 | 39 | 0.22 | |
| | 500-850 | - | 658 | 3.68 | |
| **0.1Au/1Fe/$CeO_2$-$O_2$ re-oxidized** | 20-380 | 349 | 157 | 0.88 | - |
| | 380-480 | 416 | 69.6 | 0.39 | |
| | 480-650 | 592 | 65.6 | 0.53 | |
| | 650-850 | - | 545 | 3.04 | |
| **0.5Au/1Fe/$CeO_2$** | 20-450 | 349 | 213 | 1.19 | 76.2 |
| | 450-850 | 570 | 766 | 4.28 | |
| **0.5Au/1Fe/$CeO_2$-$O_2$ re-oxidized** | 20-450 | 349 | 213 | 1.19 | - |
| | 450-850 | 570 | 766 | 4.28 | |

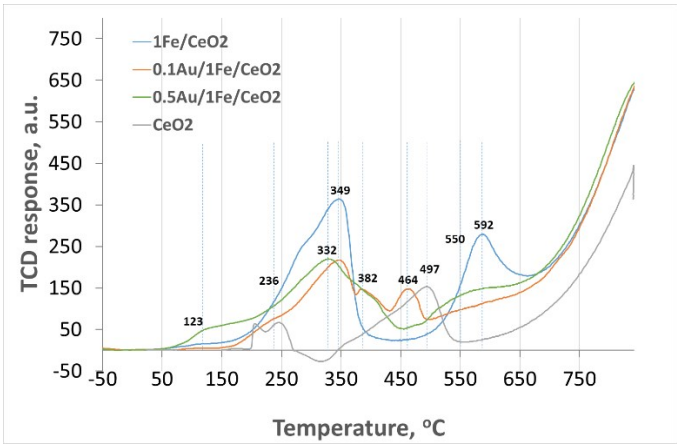


**Fig. S8**. TPR-$H_2$ data for 1Fe/$CeO_2$ (blue line), 0.1Au/1Cu/$CeO_2$ (orange line) and 0.5Au/1Cu/$CeO_2$ (green line) catalysts

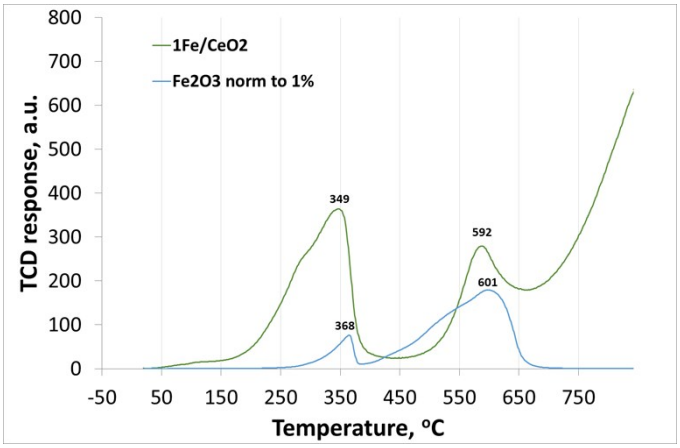


**Fig. S9.** TPR-$H_2$ data for 1Fe/$CeO_2$ and $Fe_2O_3$ normalized to 1% wt.

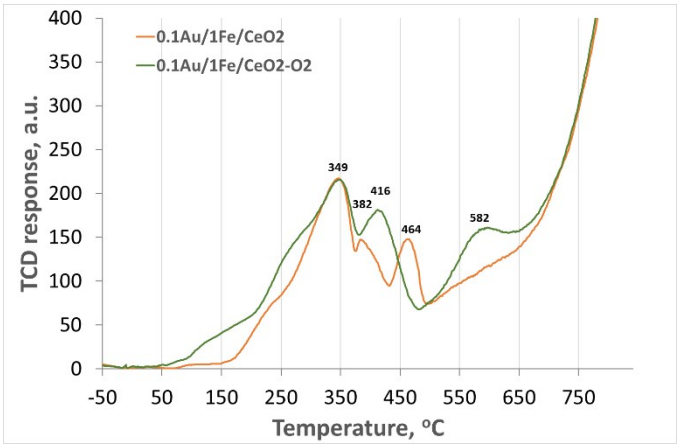


**Fig. S10**. TPR-$H_2$ data for 0.1Au/1Cu/$CeO_2$ (orange line) and 0.1Au/1Cu/$CeO_2$ catalyst re-oxidized in $O_2$/He flow at 90°C for 2 h (green line)

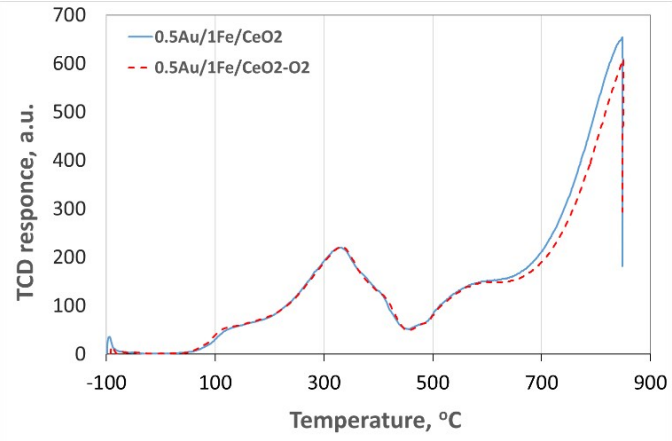


**Fig. S11**. TPR-$H_2$ curves for 0.5Au/1Cu/$CeO_2$ (blue line) and 0.5Au/1Cu/$CeO_2$ catalyst re-oxidized in $O_2$/He flow at 90°C for 2 h (red-dotted line)

## Catalytic results

**Table S6.** The activity and selectivity of the prepared catalysts.

| Entry | Sample | t, °C | p $O_2$, atm | Specific Activity on Au, $h^{-1}$ [a] | X, % | C bal,% | Selectivity, % | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | LA | AA | FA | GlyA | TA | GcA |
| 1 | 1Au/$TiO_2$ | 60 | atm | 65 | 40 | 87 | 3 | 4 | 1 | 38 | 19 | 1 |
| 2 | 0.5Au/1Fe/$TiO_2$ | 60 | atm | 48 | 15 | 100 | 16 | 0 | 23 | 28 | 0 | 32 |
| 3 | 0.1Au/1Fe/$TiO_2$ | 60 | atm | 0 | 0 | - | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | 0.5Au/1Cu/$TiO_2$ | 60 | atm | 139 | 43 | 68 | 0 | 0 | 11 | 27 | 0 | 0 |
| 5 | 1Fe/$TiO_2$ | 60 | atm | 0 | 0 | - | - | - | - | - | - | - |
| 6 | 1Cu/$TiO_2$ | 60 | atm | 0 | 0 | - | - | - | - | - | - | - |
| 7 | 0.5Au/1Fe/$TiO_2$ | 60 | 5 | 110 | 34 | 95 | 4 | 0 | 18 | 36 | 0 | 26 |
| 8 | 0.5Au/1Cu/$TiO_2$ | 90 | 5 | 68 | 66 | 63 | 0 | 0 | 20 | 12 | 0 | 12 |
| 9 | 0.5Au/1Fe/$TiO_2$ | 90 | 5 | 177 | 55 | 91 | 5 | 0 | 20 | 29 | 2 | 28 |
| 10 | 0.5Au/$TiO_2$ | 90 | 5 | 139 | 43 | 69 | 2 | 0 | 2 | 21 | 0 | 3 |
| 11 | 1Fe/$TiO_2$ * | 90 | 5 | 4 | 11 | 99 | 0 | 0 | 18 | 28 | 0 | 45 |
| 12 | 1Fe/$CeO_2$ * | 90 | 5 | 2 | 5 | 100 | 3 | 1 | 4 | 87 | 0 | 5 |
| 13 | 1Cu/$CeO_2$ * | 90 | 5 | 18 | 54 | 55 | 0 | tr | 10 | 3 | 0 | 3 |
| 14 | 1Cu/$TiO_2$ * | 90 | 5 | 20 | 45 | 64 | tr | tr | 12 | tr | 0 | 7 |
| 15 | 0.025Au/1Fe/$TiO_2$ | 90 | 5 | 1225 | 30 | 78 | 1 | 0 | 8 | 10 | 0 | 9 |
| 16 | 0.025Au/1Cu/$TiO_2$ | 90 | 5 | 1483 | 68 | 51 | 0 | tr | 19 | 8 | 0 | 0 |
| 17 | 0.025Au/1Cu/$CeO_2$ | 90 | 5 | 1547 | 78 | 40 | 0 | 0 | 23 | 0 | 0 | 0 |
| 18 | 0.025Au/1Cu/$CeO_2$ | 60 | 6 | 2256 | 35 | 76 | 0 | 0 | 31 | 0 | 0 | 0 |
| 19 | 0.025Au/$TiO_2$ | 90 | 5 | 193 | 3 | 97 | 5 | 2 | 5 | 85 | 0 | 0 |
| 20 | 0.1Au/1Fe/$TiO_2$ | 90 | 5 | 532 | 44 | 79 | 8 | 0 | 15 | 2 | 0 | 28 |
| 21 | 0.1Au/1Fe/$CeO_2$ | 90 | 5 | 661 | 48 | 90 | 9 | 1 | 4 | **53** | 8 | 4 |
| 22 | 0.1Au/1Fe/$CeO_2$ [b] | 90 | 5 | 508 | **68** | 88 | 11 | tr | 3 | **63** | 0 | 2 |
| 23 | 0.1Au/1Fe/$CeO_2$ [c] | 90 | 5 | 484 | 30 | 100 | **21** | 2 | 7 | **65** | 0 | 5 |
| 24 | 0.1Au/1Fe/$CeO_2$ [d] | 90 | 5 | 806 | 15 | 100 | 1 | 1 | 2 | 96 | 0 | 0 |
| 25 | 0.1Au/$CeO_2$ | 90 | 5 | 161 | 10 | 99 | 5 | 1 | 6 | 61 | 0 | 19 |

**Reaction conditions**: Glycerol aqua solution (Gly) 0.3M, 0.5 ml, NaOH:Gly 1.7, m cat 11 mg, 2 h; [b] 4 h; [c] recycled catalyst (second cycle) without washing, Gly 0.3 M, 1 ml, NaOH:Gly 0.9, m cat 22 mg, 2 h; [d] 0.5 h
LA – lactic acid, AA – acetic acid, FA – formic acid, GlyA – glyceric acid, GcA – glycolic acid, X – conversion, C bal. – carbon balance, tr -trace amount. [a] Specific activity on Au after 2 h of the reaction was calculated as Gly converted (mol) on Au (mol) per time (h). In the case of bimetallic catalyst Gly converted on Au was calculated as Gly converted on bimetallic catalyst abstracting the amount of Gly converted on Cu or Fe in monometallic catalysts. * Specific activity calculated for Fe or Cu catalyst after 2 h of the reaction as Gly converted (mol) on Fe or Cu (mol) per time (h).

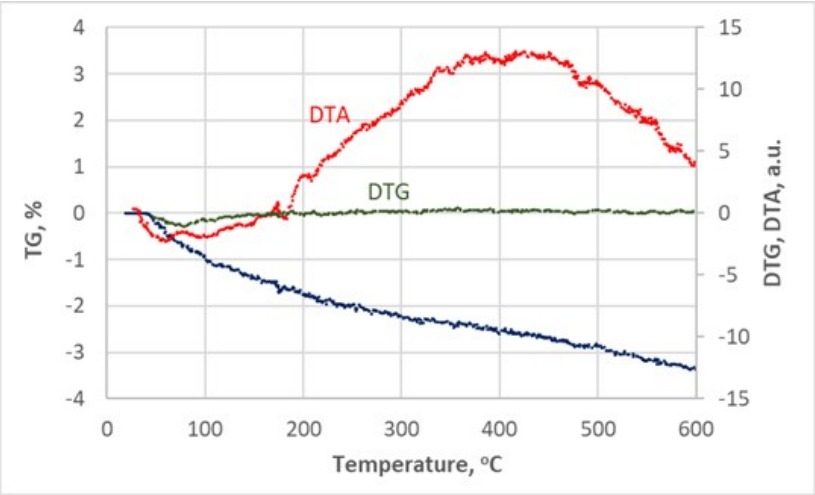


**Fig. S12.** TG-DTA analysis of spent unwashed catalyst 0.025Au/1Cu/$CeO_2$ dried in air at RT.

Thermal analysis of the sample was carried out using the combined TG-DTA method. A sample with a mass of 0.010–0.015 g was placed in a Pt crucible, and then gravimetric imaging was performed in the linear heating mode from 20 to 600 °C at a rate of 10 °C/min in air; α-$Al_2O_3$ was used as a reference.

**Table S7.** Effect of Au loading on the activity of Au/Fe/$TiO_2$ catalysts in glycerol oxidation.

| Entry | Sample | Specific Activity on Au or Fe, $h^{-1}$ | X, % |
|---|---|---|---|
| 1 | 1Fe/$TiO_2$ | 4 | 11 |
| 2 | 0.5Au/1Fe/$TiO_2$ | 68 | 66 |
| 3 | 0.1Au/1Fe/$TiO_2$ | 532 | 44 |
| 4 | 0.1Au/1Fe/$CeO_2$ | 661 | 48 |
| 5 | 0.025Au/1Fe/$TiO_2$ | 1225 | 30 |