Bifunctional Au-Sn-SiO₂ catalysts promote the direct upgrading of glycerol to methyl lactate

Margot Van der Verren,¹ Anna Corrias,² Vit Vykoukal,³ Ales Styskalik,³ Carmela Aprile,⁴ Damien P. Debecker¹ *

¹ Institute of Condensed Matter and Nanoscience (IMCN), UCLouvain, Place Louis Pasteur 1, 1348 Louvain-La-Neuve, Belgium.

² University of Kent, School of Chemistry and Forensic Science, Ingram Building, Canterbury, CT2 7NH, UK

³ Masaryk University, Department of Chemistry, Kotlarska 2, CZ-61137 Brno, Czech Republic

⁴ Université de Namur, Unit of Nanomaterial Chemistry, Department of Chemistry, Namur 5000, Belgium

*Corresponding author: <u>damien.debecker@uclouvain.be</u>

Supplementary information



Scheme S1: Schematic view of the aerosol-assisted sol-gel process



Figure S1: XPS spectra of the Au4f region of AuSiO₂. The theoretical binding energy of Au4 $f_{7/2}^{0}$ is 84.3 eV.



Figure S2: Solid state ¹¹⁹Sn static NMR spectrum of (a) pure SnO_2 , (b) $Au(1)SnSiO_2$ calcined, (c) fresh $Au(1)SnSiO_2$ and (d) $SnSiO_2$ calcined.



Figure S3: FTIR spectra after pyridine adsorption and desorption at 150 °C for 2 hours of $SnSiO_2$ (bottom green curve) and Au(1)SnSiO₂ (top red curve). B = band corresponding to Bronsted acid sites; L = band corresponding to Lewis acid sites.



Figure S4: XPS spectra of the (A) the Au4f region and (B) Sn3d region of Au(x)SnSiO2(x = 0.5% (-), 1% (-), or 2% (-)). The theoretical binding energy of Au4f_{7/2}⁰ and Sn3d_{5/2} in Sn4+ state are respectively 84.3 eV and 487.2 eV.



Figure S5: Comparison of the XRD diffractograms obtained with the monofunctional AuSiO₂ catalysts and the bifunctional Au(x)SnSiO₂ catalysts (x = 0.5% (-), 1% (-), or 2% (-)). The presence of the small shoulder at ~41° in the bifunctional catalyst is noticed but can not be interpreted at this stage.



Figure S6: Gold nanoparticles size distribution of (A) $Au(0.5)SnSiO_2$, (B) $Au(1)SnSiO_2$ and (C) $Au(2)SnSiO_2$. TEM micrographs are shown as representative images of the samples used to count and measure nanoparticles size; the size distribution was estimated by measuring ~200 nanoparticles.



Figure S7: Kinetic study of the transformation glycerol (GLY) to methyl lactate (ML), methyl glycerate (MGE) and methyl glycolate (MGO) with (A) Au(0.5)SnSiO2 and (B)Au(2)SnSiO2. Reaction conditions: $T = 160^{\circ}$ C, pair = 15 bars, 0.125 M glycerol in methanol, and GLY/Catalyst ratio = 1.15 (w/w). Each measure has an error of \pm 5%.



Figure S8: Hot filtration test performed with Au(1)SnSiO₂.



Figure S9: Recycling test performed with $Au(1)SnSiO_2$. The Au/GLY ratio was maintained constant in each cycle.

Temperature (°C)	P _{air} (bars)	Gly/Au	GLY conversion	ML Selectivity	ML Yield
		(w/w)	(%)	(%)	(%)
160	15	1.15	85	73.1	62.2
160	30	1.15	77.5	72.9	56.5
160	30	0.575	69.5	75.2	52.2
160	30	2.3	77.2	67.6	52.2
160	30	4.6	54	54.3	29.3

Table S1: Catalytic performance of Au(1)SnSiO₂ on different reaction conditions.

120	30	2.3	5	100	5
140	30	2.3	41.2	66.9	27.7
180	30	2.3	96.4	60	57.8

One parameter is change at the time. Increasing the amount of air (and therefore the amount of oxidant in the reactor) did not improve the catalytic performance of $Au(1)SnSiO_2$. Similarly, increasing the amount of glycerol does not have a significant impact to a certain point (GLY/Au (w/w) = 4.6) where the ML yield starts to decrease. The diminution of temperature leads to the gradual loss of activity, while increasing the temperature reduced the selectivity to ML.

References

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