Supplementary Information

Gold Catalysis for Selective Hydrogenation of Aldehydes and Valorization of Bio-Based Chemical Building Blocks

Rerison J. M. Silva,[a] Jhonatan L. Fiorio,[a] Pedro Vidinha[a] and Liane M. Rossi *,[a]

[a]*Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, 05508-000 São Paulo-SP, Brazil*

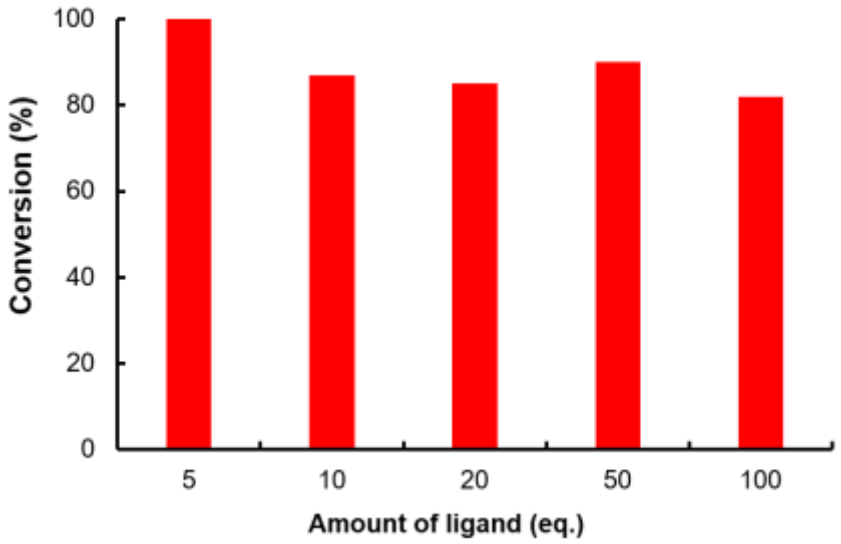

Figure S1. Effect of the amount of ligand (L3) on the hydrogenation of benzaldehyde **1a** catalyzed by Au / SiO_2. Reaction conditions: 1 mmol of aldehyde, 0.01 mmol of Au, ligand, 2 mL of *i*-PrOH, 100 °C, 6 bar of H_2, 24 h. Conversion and selectivity were determined by GC analysis using biphenyl as an internal standard.

*e-mail: lrossi@iq.usp.br

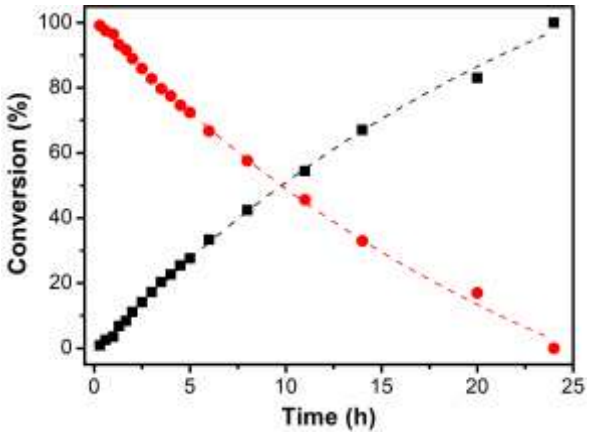

Figure S2. Kinetic data of the hydrogenation of benzaldehyde **1a** catalyzed by Au / SiO_2. Reaction conditions: 1 mmol of aldehyde, 0.01 mmol of Au, 0.05 mmol of ligand L3, 2 mL of *i*-PrOH, 100 °C, 6 bar of H_2, 24 h.

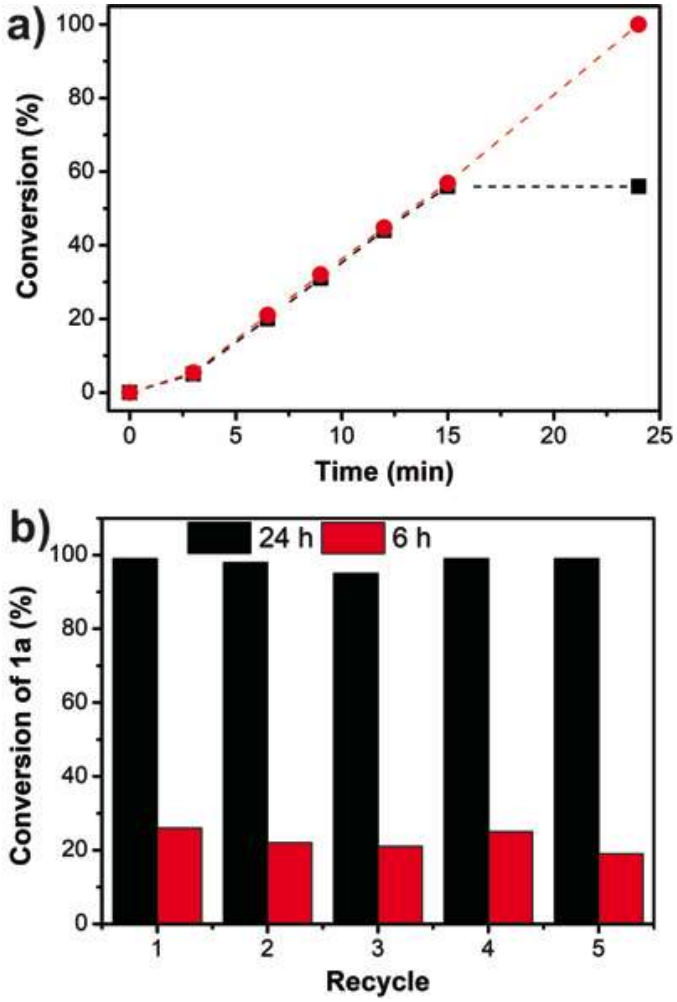

Figure S3. (a) Hot filtration test and (b) recycle experiment of the hydrogenation of benzaldehyde **1a** catalyzed by Au / SiO_2 + L3 catalyst systems. New portions of ligand were added in the recycling reaction. Reaction conditions: 1 mmol of aldehyde, 0.01 mmol of Au, 0.05 mmol of ligand, 2 mL of *i*-PrOH, 100 °C, 6 bar of H_2, 24 h.

Table S1. Summary of results reported for hydrogenation of aldehydes catalyzed by heterogeneous gold-based catalyst[a]

Catalyst	Condition	Hydride source	TOF / h^{-1}	Reference
Au / SiO_2	6 bar H_2, 80 °C, 2,4,6-trimethylpyridine, 24 h, *i*-PrOH	H_2	4.2	this work
Au / SiO_2	20 bar H_2, 100 ºC, 2,4,6-trimethylpyridine, 24 h, *i*-PrOH	H_2	9.6	this work
Au@N-doped carbon / TiO_2	20 bar H_2, 80 °C, 24 h, *i*-PrOH	H_2	2.1	this work
Au^0 / nano-ZnO	40 bar H_2, 60 °C, DMF, 24 h	H_2	7.1	1
SPO AuNPs	40 bar H_2, 60 °C, THF, 18 h	H_2	22	2
AuNPore	Et_3SiH, H_2O, Et_3N, acetonitrile, 70 ºC, 24 h	Et_3SiH	2.1	3
$Au_{>99}Ag_1$NPore	8 bar H_2, 90 °C, triethylamine, 24 h	H_2	0.83	4
$Au_{11}(PPh_2Py)_7Br_3$ / CeO_2	10 bar H_2, H_2O, 80 °C, 10 h	H_2	9.8	5
$Au_{25}(SR)_{18}$ / CeO_2	18 bar H_2, H_2O, pyridine, $CoCl_2$, 50 °C, 10 h	H_2	20	6
Au@CeO_2 / HT	30 bar H_2, toluene, 120 °C, 25 h	H_2	2.8	7

[a]The TOF value was calculated in the format of mol **1a** mol^{-1} metal h^{-1}. The amount of metal is based on the moles of metal components involved. TOF: turnover frequency; DMF: dimethylformamide; SPO: secondary phosphine oxide; NPs: nanoparticles; THF: tetrahydrofuran; AuNPore: gold nanopore; SR: thiolate ligand (R: C_2H_4Ph); HT: hydrotalcite.

References

1. Mertens, P. G. N.; Wahlen, J.; Ye, X.; Poelman, H.; De Vos, D. E.; *Catal Lett.* **2007**, *118*, 15.
2. Cano, I.; Chapman, A. M.; Urakawa, A.; van Leeuwen, P. W. N. M.; *J. Am. Chem. Soc.* **2014**, *136*, 2520.
3. Takale, B. S.; Wang, S.; Zhang, X.; Feng, X.; Yu, X.; Jin, T.; Bao, M.; Yamamoto, Y.; *Chem. Commun.* **2014**, *50*, 14401.
4. Takale, B. S.; Feng, X.; Lu, Y.; Bao, M.; Jin, T.; Minato, T.; Yamamoto, Y.; *J. Am. Chem. Soc.* **2016**, *138*, 10356.
5. Liu, C.; Abroshan, H.; Yan, C.; Li, G.; Haruta, M.; *ACS Catal.* **2016**, *6*, 92.
6. Li, G.; Abroshan, H.; Chen, Y.; Jin, R.; Kim, H. J.; *J. Am. Chem. Soc.* **2015**, *137*, 14295.
7. Urayama, T.; Mitsudome, T.; Maeno, Z.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K.; *Chem. Eur. J.* **2016**, *22*, 17962.