Electronic Supplementary Information for

Production of γ-Valerolactone from Biomass-derived Compounds using Formic Acid as a Hydrogen Source over Supported Metal Catalysts in Water Solvent

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Preparation of ordered mesoporous silica (SBA-15)

Besides some available support materials such as metal oxide, silica, and carbon, the ordered mesoporous material also becomes good support because of its high surface area and thermal stability. The thermal stability makes SBA is not destroyed in regeneration process using calcination method. This is the brief procedure for preparation of mesoporous material SBA-15: 2 g of P123 was dissolved with 15 mL of water and stirred at 40 °C for 3 h. Subsequently, 35 mL of 2 M HCl was introduced and continued to stir 20 min followed by addition of 5 mL of TEOS 98% into the solution. The mixture was kept under the same conditions for 24 h for pre-hydrolysis before transferred to a teflon-lined steel autoclave and heated at 100 °C for 24 h. After filtration and wash with water, the obtained solid was calcined at 500 °C for 5 h.

Preparation of zirconium carbonate (ZrC)

40 mL of 0.5 M $ZrOCl_2 \cdot 8H_2O$ solution (A) and 100 mL of 0.25 M Na_2CO_3 solution (B) were prepared in individual flasks. The solution (A) was added slowly into the solution (B) by a peristaltic pump with rate of 1 mL min^{-1}. The obtained white gel was aged at 70 ^oC for 12 h, then the solid was recovered by filtration, washed with 1000 mL of distilled water (till the pH of filtrate reached *ca.* 7) and dried at 150 ^oC for 3 h.

Table S1. Various metals supported on zirconia for hydrogenation of LA

Entry	Catalyst	GVL Yield (%)
1	Au/ZrO_2	48
2	Ru/ZrO_2	2
3	Fe/ZrO_2	1
4	Co/ZrO_2	1
5	Ni/ZrO_2	1
6	Cu/ZrO_2	1
7	Ag/ZrO_2	1

Reaction conditions: LA (2 mmol), FA (4 mmol), 5wt% supported metal catalyst (0.02 g), water (1 mL), temperature (150 °C), time (5 h).

Table S2. Decomposability of FA over Ru/C and Au/ZrO_2 in hydrogenation reaction of LA

Entry	Catalyst	FA amount (mmol)	FA decomposition (%) [a]
1	5wt% Ru/C	2	56
2		4	49
3		6	43
4	5wt% Au/ZrO_2	2	100
5		4	100
6		6	100

Reaction conditions: LA (2 mmol), catalyst (0.02 g), water (1 mL), temperature (150 °C), time (5 h). [a]Estimated by HPLC.

Table S3. Hydrogenation of LA over various contents of gold on zirconia

Entry	Catalyst	Actual metal content (wt%)[a]	GVL Yield (%)	TON[b]
1	1wt% Au/ZrO_2	1.01	14	276
2	2wt% Au/ZrO_2	1.89	36	355
3	3wt% Au/ZrO_2	3.02	96	630
4	4wt% Au/ZrO_2	3.89	97	478
5	5wt% Au/ZrO_2	4.89	97	382

Reaction conditions: LA (2 mmol), FA (4 mmol), catalyst (0.02 g), water (1 mL), temperature (150 °C), time (5 h). [a]Determined by ICP. [b]Turnover number (TON) is defined as mole of formed GVL per actual mole of supported metal.

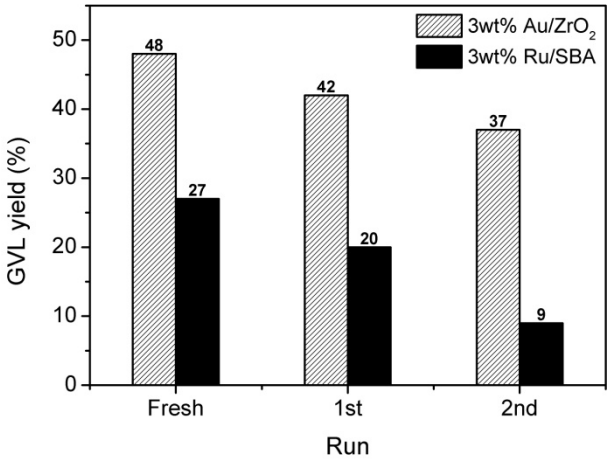

Figure S1. Recylability of 3wt% Au/ZrO_2 and 3wt% Ru/SBA in dehydration/hydrogenation reaction of fructose to produce GVL.
Reaction conditions: Fructose (2 mmol), FA (4 mmol), catalyst (0.02 g), water (1 mL), temperature (150 °C), time (5 h).