Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

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Hydrogen-Independent Reductive Transformation of Carbohydrate Biomass into γ-Valerolactone and Pyrrolidone Derivatives with Supported Gold Catalysts**

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1. Materials and Methods

1.1 Materials

Levulinic acid (LA, 98 %), γ-valerolactone (GVL, 98 %), formic acid (FA, 97 %), fructose (99 %), glucose (99 %), sucrose (99 %), starch (soluble), cellulose (microcrystalline), aniline (99 %), benzylamine (98 %), cyclohexylamine (98 %), hexylamine (99 %), 4-methylaniline (99 %), 4-methoxyaniline (99 %), 4-chloroaniline (98 %), glycerol (99 %), 1,2-propanediol (99.5 %), 1,4-butanediol (99 %) were supplied by Alfa Aesar.

Gold catalysts including 4.5 wt% Au/Fe_2O_3 (type C, lot no. Au/Fe_2O_3 no. 02-5) and 0.8 wt% Au/C (type D, lot no. Au/C no. 38D) were supplied by the World Gold Council (WGC). 1 wt% Au/TiO_2 (Catalogue number 79-0165), 1 wt% Au/ZnO (catalogue number 79-0170) and 1 wt% Au/Al_2O_3 (catalogue number 79-0160) were supplied by Mintek. 5 wt% Pd/C (stock # 38300) and 5 wt% Ru/C (stock # 11748) were supplied from Alfa Aesar.

1.2 Catalyst preparation

Preparation of ZrO_2 supports: ZrO_2 powders were prepared by a conventional precipitation method following the reported procedure.[S1] Briefly, 12.9 g $ZrOCl_2 \cdot 8H_2O$ was dissolved in 200 mL deionized water at room temperature, the pH was adjusted to 9.0 by dropwise addition of NH_4OH (2.5 M). The resultant hydro gel was washed with deionized water until free of chloride ions. The precipitate was then dried at 110 ^oC overnight and calcined at 400 ^oC for 2 h in air. The BET surface area of the resultant material was 110 m^2 g^{-1} (Micromeritics TriStar 3000). The crystal phase of ZrO_2 was composed of 56 % monoclinic phase and 44 % tetragonal phase (based on XRD analysis, see Figure S2).

Preparation of Au/ZrO_2-VS catalyst: Au/ZrO_2-VS catalysts were prepared by a modified deposition-precipitation (DP) method by mixing ZrO_2 powders (2 g) with appropriate amounts of aqueous solutions of chloroauric acid (100 mL, 1 mM), the pH was adjusted to 9.0 by dropwise addition of 0.25 M NH_4OH. After 6 h stirring at room temperature the catalyst was washed five times with deionized water and separated by filtration. The samples were dried at 110 ^oC in a forced air oven for 1 h, followed by reduction with a stream of 5 vol% H_2/Ar at 350 ^oC for 2 h. The BET surface area of the resultant Au/ZrO_2-VS catalyst was 113 m^2 g^{-1}. The crystal phase of the final catalyst was composed of 62 % monoclinic phase and 38 % tetragonal phase (based on XRD analysis, see Figure S2). The concentration of gold was 0.8 % Au by weight (ICP-AES). A large fraction of the Au particles in this catalyst was within 1.2~2.5 nm in diameter (TEM in Figure S1). XPS measurements showed that all the gold in the catalyst was in its metallic state (Figure S3).

Preparation of Au/SiO_2 catalyst: 1.0 wt% Au/SiO_2 catalysts were prepared by following the modified DP procedure as described above. 2.0 g of SiO_2 (Degussa, Aerosil 380, specific surface area: 380 m^2 g^{-1}) was introduced into the appropriate amount of $HAuCl_4$ solution in order to prepare catalysts with 1.0 wt% gold content. After stirring at 75 ^oC for 1 h the solution was cooled down to room temperature and 0.2 M NH_4OH was added to the solution under stirring. After 6 h stirring at room temperature the catalyst was washed five times with deionized water and separated by centrifugation. The samples were dried at 110 ^oC in a forced air oven for 1 h and reduced in flowing 5 vol% H_2/Ar at 350 ^oC for 2 h.

Preparation of Au/ZrO_2 and Au/CeO_2 catalysts: 1.0 wt% Au/ZrO_2 and Au/CeO_2 catalysts were prepared by a routine DP method as developed by Haruta et al.[S2] An appropriate amount of aqueous solutions of chloroauric acid ($HAuCl_4$) was heated to 80 ^oC under vigorous stirring. The pH was adjusted to 9.0 by dropwise addition of NaOH (0.2 M), and then 1.0 g of ZrO_2 or CeO_2 was dispersed in the solution. The mixture was stirred for 2 h at 80 ^oC, after which the suspension was cooled to room temperature. Extensive washing with deionized water was then followed until it was free of chloride ions. The samples were dried at 110 ^oC in a forced air oven for 1 h, followed by calcination in air at 350 ^oC for 2 h.

Preparation of Pt/ZrO_2, Ru/ZrO_2 and Pd/ZrO_2 catalysts: 1 wt% Pt/ZrO_2, Ru/ZrO_2 and Pd/ZrO_2 catalysts were prepared by an incipient wetness technique. ZrO_2 (1.0 g as prepared ZrO_2) was added to 1 mL of an aqueous solution containing appropriate amounts of $H_2PtCl_6 \cdot 6H_2O$, $RuCl_3$ or $PdCl_2$. After a perfect mixing of the corresponding slurries, the samples were dried under vacuum at room temperature for 12 h and then reduced in 5 vol% H_2/Ar at 400 ^{o}C for 2 h.

1.3 Catalyst characterization

BET analysis: The BET specific surface areas of the prepared catalysts were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. Sample degassing was carried out at 300 ^{o}C prior to acquiring the adsorption isotherm.

X-ray diffraction (XRD) analysis: The crystal structures of ZrO_2 were characterized with powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu Kα radiation source at 40 kV and 40 mA. The percentage of monoclinic phase (M %) in the oxide “support” was measured according to the equation:[S3] M % = $I_{M(\bar{1}11)} / 1.6 I_{M(\bar{1}11)} + I_{T(111)}$, where $I_{M(\bar{1}11)}$ and $I_{T(111)}$ are the integrated intensities of the monoclinic ($\bar{1}11$) ($2\theta = 28.5^{o}$) and tetragonal (111) ($2\theta = 30.4^{o}$) planes, respectively.

Elemental analysis: The Au loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer.

Transmission electron microscopy (TEM): TEM images for supported gold catalysts were taken with a JEOL 2011 electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the samples dispersed with ethanol were deposited onto a carbon-coated copper grid and then quickly moved into the vacuum evaporator. The size distribution of the metal nanoclusters was determined by measuring about 200 random particles on the images.

X-ray photoelectron spectroscopy (XPS): XPS analysis was performed using a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The Mg Kα (hν = 1253.6 eV) was operated at 15 kV and 20 mA. The energy scale was internally calibrated by setting the C 1s peak at 284.6 eV.

2. Catalytic activity measurements

2.1 Catalytic conversion of LA and FA into GVL

A mixture of LA (18 mmol), FA (18 mmol), supported metal catalysts (metal 0.1 mol%), 2-methoxyethyl ether (9 mmol, internal standard), water (40 mL) were charged into a 50-mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm under 0.5 MPa N_2 atmospheres for given reaction time. The mixture of substrates and catalyst were heated to the desired temperature in less than 15 minutes. The liquid products were analyzed on a Shimadzu GC-17A gas chromatograph equipped with a capillary column HP-FFAP (30 m × 0.25 mm) and FID detector. The identification of the products was performed by using a GC-MS spectrometer. To verify whether there is any leaching of gold or zirconium during the catalytic reductive conversion of LA in concentration solution (Table 1, entry 8), the Au/ZrO_2-VA was removed from the reaction mixture by filtration after 6 h reaction. Analysis of the filtrate by inductive coupled plasma emission spectroscopy (ICP) showed no detectable leaching of Au or Zr (< 2.5 ppb) into the solution.

2.2 Recovery and reuse of Au/ZrO_2-VS

First, 1.772 g fresh Au/ZrO_2-VA catalyst (72 μmol Au) was used in a mixture containing 72 mmol LA, 72 mmol FA and 160 mL water in 200 mL high pressure reactor. The reaction was performed according to Section 2.1. After finishing the reaction, the catalyst was recovered, filtered and washed three times with distilled water. Then, they are dried under vacuum at room temperature for 12 h to obtain the 1st re-use catalyst. Second, 1.329 g 1st re-use catalyst (54 μmol Au) was used in a mixture containing 54 mmol LA, 54 mmol FA and 120 mL water in 150 mL high pressure reactor. Repeat the recovery process to get the 2nd re-use bath. Then, 0.886 g 2nd re-use catalyst (36 μmol Au) was used in a mixture containing 36 mmol LA, 36 mmol FA and 80 mL water in 100 mL high pressure reactor, 0.443 g 3rd re-use catalyst (18 μmol Au) was used in a mixture containing 18 mmol LA, 18 mmol FA and 40 mL water in 50 mL high pressure reactor and 0.222 g 4th re-use catalyst (9 μmol Au) was used in a mixture containing 9 mmol LA, 9 mmol FA and 20 mL water in 25 mL high pressure reactor. After five times (using the 4th re-used catalyst for the fifth reaction), the Au/ZrO_2-VS catalyst still remain highly active (Table 1, entry 2). Moreover, XRD patterns indicated that the crystallinity of recycled Au/ZrO_2-VS sample (after five runs) is the same as that of the fresh sample, showing that the support structure is retained in the reduction process.

2.3 Sole decomposition of formic acid or LA

A mixture of FA (18 mmol), supported metal catalysts (metal 0.1 mol%), water (40 mL) were charged into a 50-mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm under 0.1 MPa He atmospheres for given reaction time. The mixture of substrate and catalyst were heated to 150 °C in less than 15 minutes. After the reaction, the concentration of residual FA was analyzed by by a HPLC (HP 1100, Agilent, USA) system consisting of a Platisil ODS C18 column and a refractive index detector. H_2SO_4 (0.5 mM) was used as the mobile phase at a flow rate of 1 mL min^{-1}. Both of the column temperature and the detector temperature were 40 °C. The gaseous products were analyzed by a gas chromatography (GC) analyzer equipped with a TDX-01 column and a thermal conductivity detector (TCD) detector. The carrier gas is helium. A standard gas sample comprising of 33.3 vol% H_2, 33.3 vol% CO and 33.3 vol% CO_2 was used to calibrate the GC. The composition of gaseous products was determined according to the standard gas. The concentration of CO was calculated according the following equation:

$$C_{CO} = \frac{f_{CO}A_{CO}}{f_{CO}A_{CO} + f_{CO_2}A_{CO_2} + f_{H_2}A_{H_2}}$$

f : gas calibration factor
A : gas peak area

To check whether there is any decomposition of LA in the absence of FA with Au/ZrO_2-VS, a mixture of LA (18 mmol), Au/ZrO_2-VS catalyst (Au 0.1 mol%), water (40 mL) were charged into a 50-mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm under 0.1 MPa N_2 atmospheres at 150 °C. The concentration of LA was constant after 6 hours reaction, verifying that the aqueous LA alone was very stable under the examined conditions.

2.4 Dehydration of carbohydrate biomass with H_2SO_4 and subsequent hydrogenation

10.8 g Carbohydrate: cellulose, starch, sucrose, glucose, or fructose was loaded in a teflon-lined stainless steel autoclave (100 mL), then 60 mL 0.5 M H_2SO_4 was added as well. The autoclave was heated to 170 °C quickly under vigorous stirring for 1 h. After the reaction, the resultant mixture was partially neutralized to a pH of 2 by adding suitable amount of CaO (the addition of CaO was to remove residual H_2SO_4 and the product of $CaSO_4$ could be used in cement industry and as soil conditioner) followed by filtration.[S4] Then the hydrolysis-derived products containing LA and formic acid (42 mL) was transferred to the 50-mL Hastelloy-C high pressure Parr reactor containing Au/ZrO_2-VS catalyst (Au 0.1 mol%) and heated to 150 °C with 0.5 MPa N_2 for 8 h. Finally the products were analyzed by a HPLC (HP 1100, Agilent, USA) system consisting of a Platisil ODS C18 column and a refractive index detector. H_2SO_4 (0.5 mM) was used as the mobile phase at a flow rate of 1 mL min^{-1}. Both of the column temperature and the detector temperature were 40 °C.

2.5 General procedure for the production of pyrrolidones by reductive amination of LA with amines and FA

A mixture of LA (8 mmol), FA (8 mmol), amine (8 mmol), Au/ZrO_2-VS catalyst (Au 0.05 mol%), H_2O (0.56 mL), and 2-methoxyethyl ether (8 mmol, internal standard) were placed into a 50-mL Hastelloy-C high pressure Parr reactor. The resulting mixture was vigorously stirred at 130 °C under N_2 atmospheres (0.5 MPa) for given reaction time at a stirring speed of 800 rpm. The product was identified by GC-MS. The conversion and product selectivity were determined by a gas chromatograph (Shimadzu GC-17A) equipped with a HP-FFAP column (30 m × 0.25 mm) and a flame ionization detector (FID).

2.6 Chemoselective hydrogenolysis of glycerol to 1,2-propanediol with formic acid

Aqueous glycerol solution (6 mL, 10 wt%), FA (26 mmol), Au/ZrO_2-VS (Au 1.0 mol%) were added to a 50-mL Hastelloy-C high pressure Parr reactor. The resulting mixture was vigorously stirred at 180 ^{o}C under N_2 atmospheres (0.5 MPa) for given reaction time. After the reaction, the liquid products were analyzed using a gas chromatograph (Shimadzu GC-17A) equipped with a HP-FFAP column (30 m × 0.25 mm) and a flame ionization detector (FID). *t*-Butanol was used as external standard for analysis. The gaseous products were collected in a gasbag and analyzed by another gas chromatography (GC) equipped with a TDX-01 column and a thermal conductivity detector (TCD) detector. The carrier gas is helium. The carbon balance of the analysis was generally within 100 ± 5%.

3. Au dispersion and specific activity of the Au/ZrO_2-VS catalyst

The values of Au dispersion can be calculated according to the simple model of hemispherical particles. The total surface area, and the number of exposed atoms, at a given metal amount, is in inverse proportion with particle diameter. (see G. C. Bond, D. T. Thompson, *Catal. Rev.-Sci. Eng.* **1999**, *41*, 319.)

The number of gold particles $N_1 = \dfrac{m_{Au}}{\frac{2}{3}\pi(\frac{d_{Au}}{2})^3\rho_{Au}}$

The gold particle diameter (d_{Au}) of this catalyst is 1.8 nm

ρ_{Au} = 19.3×10^3 kg m^{-3}

The overall surface area of gold particles $S = 2\pi(\frac{d_{Au}}{2})^2 N_1$

Dispersion $D = \dfrac{N_S}{N_T} = \dfrac{Sk}{n_{Au}N_A}$

N_S = total number of surface gold atoms

N_T = total number of gold atoms

The gold atom density (k) is 1.15×10^{19} m^{-2}

$N_A = 6.02\times10^{23}$ mol^{-1} $n_{Au} = m_{Au}/M_{Au}$

Assuming the case of Au/ZrO_2-VS, D_{Au} = 64 %

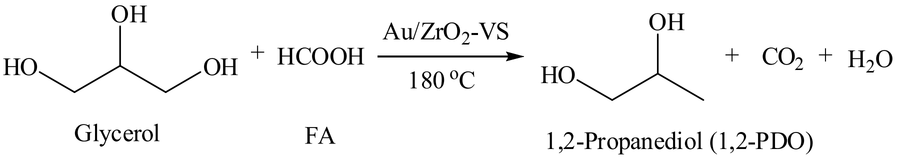
Accordingly, the total turn over number (TON) for LA conversion (five successive runs) base on surface metal atoms (Au) is 7600. For the detail of calculation please refer to the reference S5.

Table S1 : Comparison of Au/ZrO_2-VS with other reported catalysts for reductive transformation of LA into GVL using 1 equiv FA as hydrogen source at 150 °C.

Entry	Catalyst	metal % (mol)	t (h)	Conversion (mol %)	Selectivity (mol %)	TON[a]
1	Au/ZrO_2-VS	0.1	30	>95%	99	7600 (4864)[b]
2[S6]	$RuCl_3/PPh_3$	0.1	36	>80%	99	2520[c]
3[S7]	Ru-P/SiO_2	0.075	12	96	99	1280

[a] The total turnover number (TON) is calculated on the basis of surface gold atoms estimated by the model of hemispherical ball. Numbers in parenthesis refer to the TON estimated on the basis of total gold atoms. [b] Calculated for five successive runs. [c] Calculated for three successive runs.

Table S2 : Chemoselective hydrogenolysis of glycerol to 1,2-propanediol in the presence of FA with Au/ZrO_2-VS catalyst.[a]



Entry	t (h)	Glycerol conversion (%)	Liquid yield (%)	Selectivity of liquid products (%)		
				1,2-PDO (%)[b]	EG (%)	CH_3OH (%)
1	1	55	41	97	2	1
2	3	71	57	97	2	1
3	6	81	67	97	2	1
4	9	90	77	96	3	1
5	12	100	88	95	1	1
6[c]	16	100	85	94	5	1

[a] Reaction conditions: 10 wt% glycerol (6 mL), FA (26 mmol), Au (1.0 mol%), 180 °C, N_2 (0.5 MPa). [b] The main product in the liquid phase was 1,2-PDO, and small amounts of ethylene glycol (EG) and methanol resulting from the cracking of carbon-carbon bond in the glycerol molecule were also detected. [c] Reaction conditions: 30 wt% glycerol (6 mL), FA (78 mmol), Au (1.0 mol%), 180 °C, N_2 (0.5 MPa). The undesired glycerol reforming products are H_2, CO and CO_2.

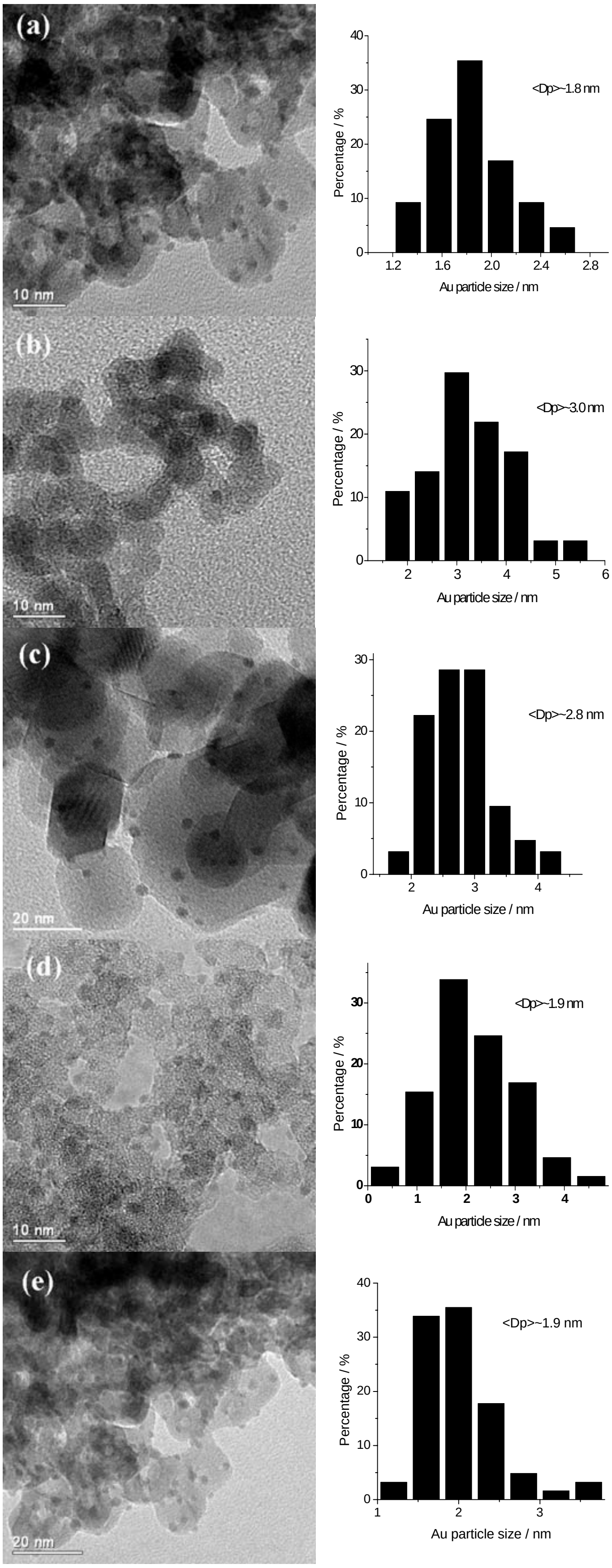


Fig S1. TEM image and gold particle size distribution of a) Au/ZrO$_2$-VS; b) Au/ZrO$_2$; c) Au/TiO$_2$; d) Au/SiO$_2$; e) Au/ZrO$_2$-VS (after five runs).

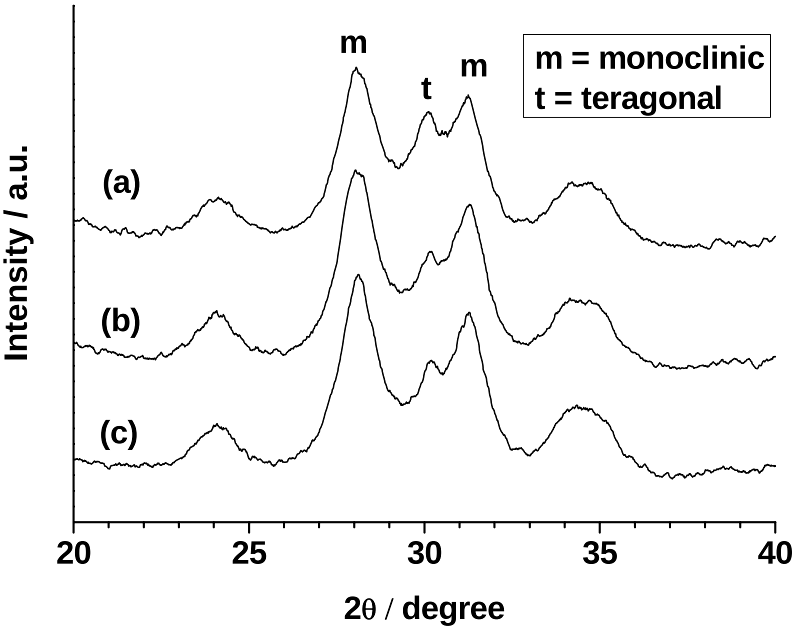


Fig S2. X-ray diffraction (XRD) patterns for (a) ZrO_2; (b) fresh Au/ZrO_2-VS catalyst; (c) the recycled Au/ZrO_2-VS, after five runs of catalysis under conditions of entry 2 in Table1. Note that the deposition of gold results in a slight phase transformation of ZrO_2 from tetragonal to monoclinic phase in the Au/ZrO_2-VS sample.

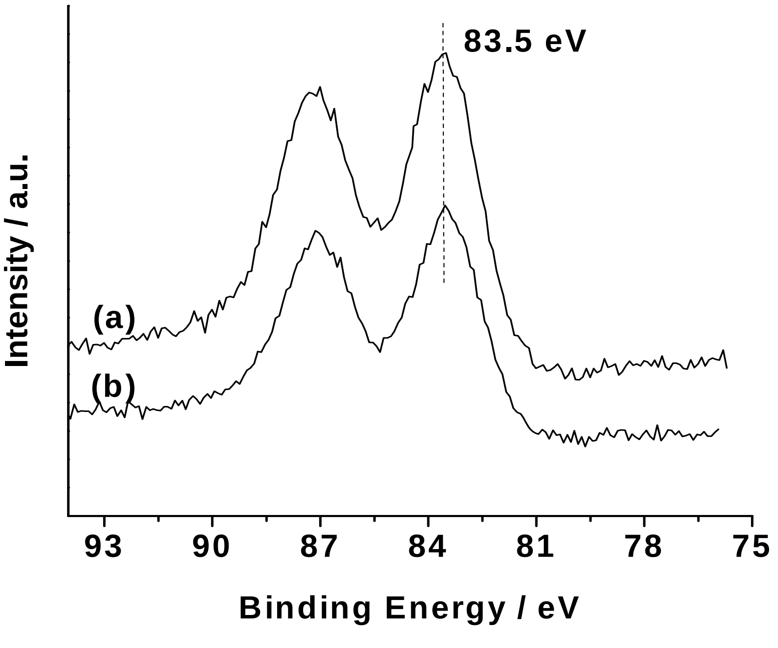


Fig S3. XPS of Au/ZrO_2-VS: (a) before reaction; (b) after five runs. The binding energy of Au $4f_{7/2}$ for Au/ZrO_2-VS is ca. 83.5 eV. Note that the metallic state of Au practically undergoes no change after the five successive runs.

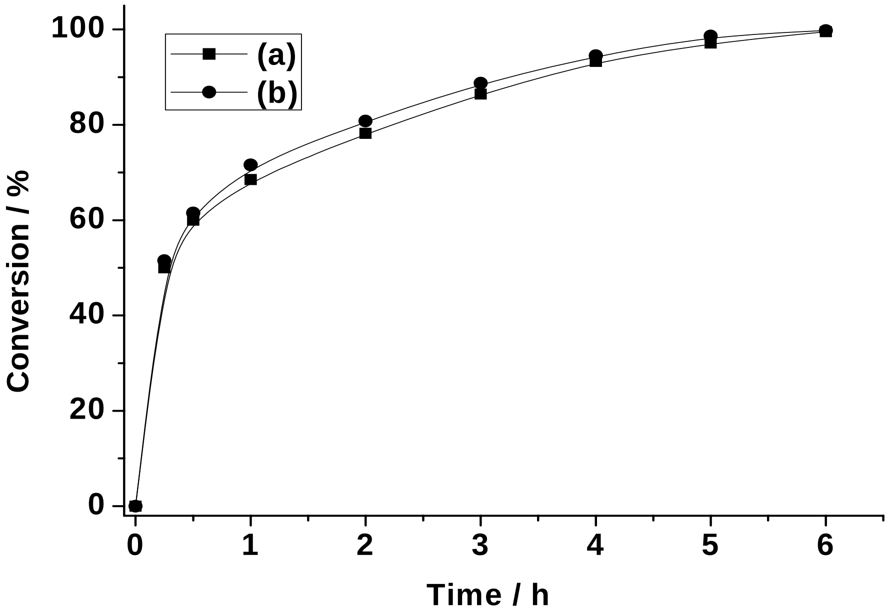


Fig S4. Reduction of LA with Au/ZrO_2-VS catalyst in the presence of a) FA; b) H_2. Reaction conditions: (a) 150 °C, LA (18 mmol), FA (18 mmol), Au (0.1 mol%), water (40 mL), N_2 (0.5 MPa); (b) 150 °C, LA (18 mmol), H_2 (4 MPa at room temperature, equivalent to the stoichiometric amount of H_2 resulting from complete decomposition of 18 mmol FA), Au (0.1 mol%), water (40 mL), N_2 (0.5 MPa).

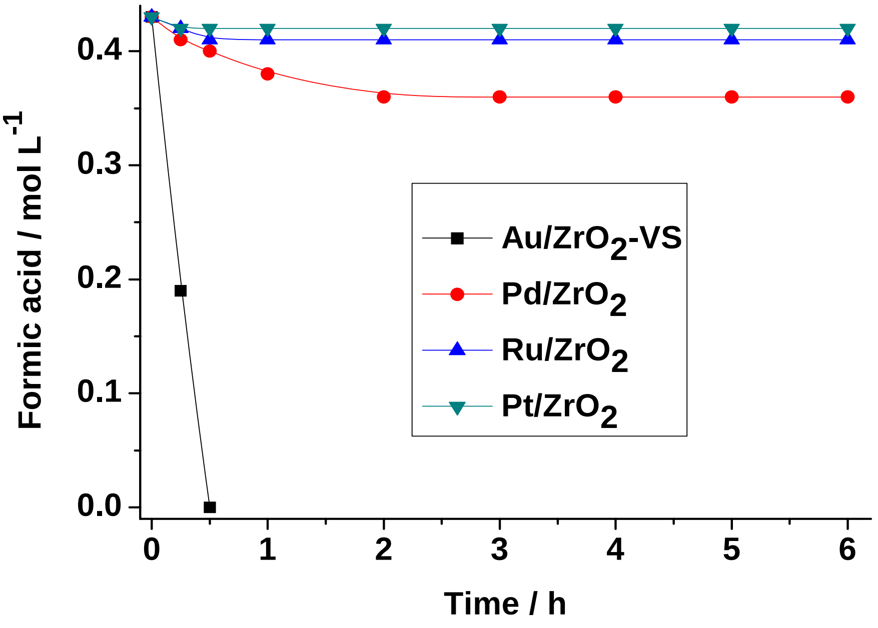


Fig S5. Decomposition of FA in the presence of LA. Reaction conditions: 150 °C, FA (18 mmol), LA (18 mmol), metal (0.1 mol%), water (40 ml). The concentration of residual FA was analyzed by HPLC.

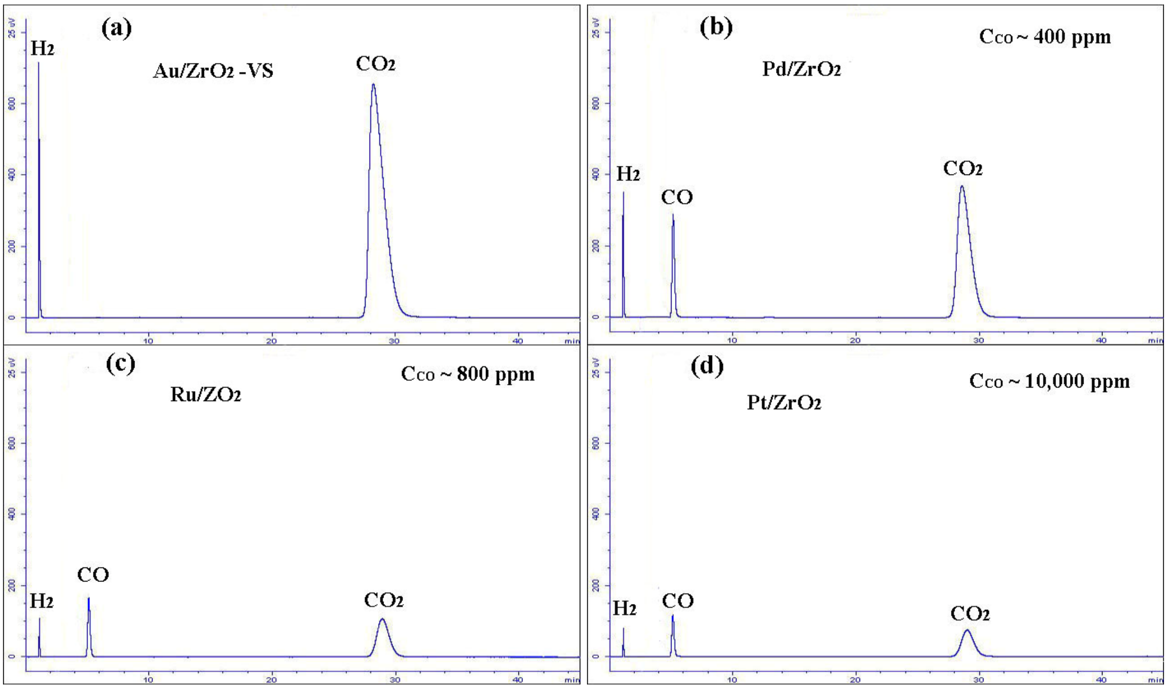
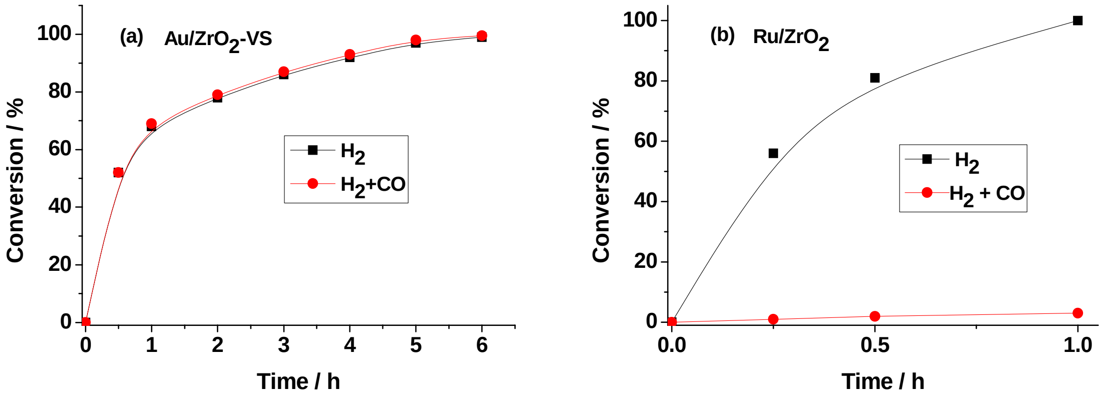


Fig S6. Gas chromatogram of the gas evolved from sole decomposition of formic acid with (a) Au/ZrO_2-VS; (b) Pd/ZrO_2; (c) Ru/ZrO_2; (d) Pt/ZrO_2. Reaction conditions: FA (18 mmol), metal (0.1 mol%), water (40 mL), He (0.1 MPa), 150 °C, 6 h.



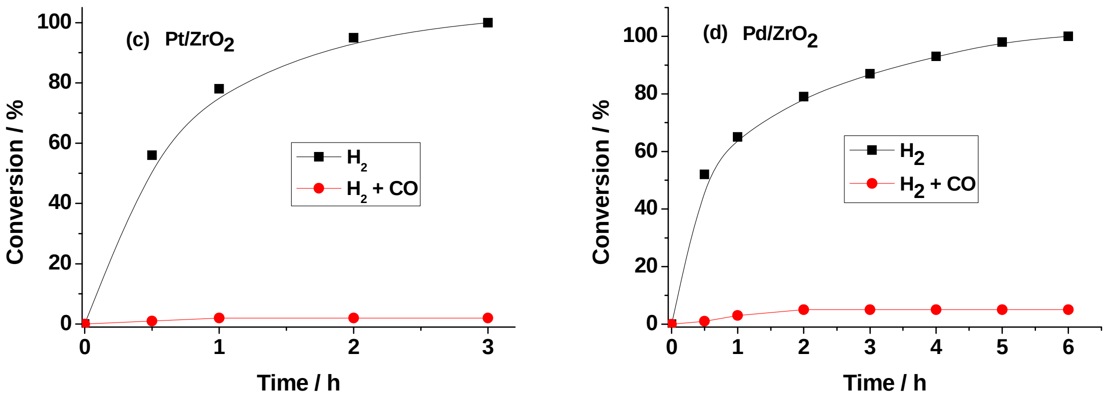


Fig S7. Effect of CO on the hydrogenation of LA over various ZrO_2 supported metal catalysts. Reaction conditions: LA (18 mmol), metal (0.1 mol%), water (40 mL), N_2 (0.5 MPa), 150 °C, and H_2 (4 MPa at room temperature, equivalent to the amount of H_2 generated from decomposition of 18 mmol FA). Reaction conducted in the absence of CO (black) and in the presence of 1,000 ppm CO (red). (a) Au/ZrO_2-VS; (b) Ru/ZrO_2; (c) Pt/ZrO_2; (d) Pd/ZrO_2. Based on above data we can conclude that the small amount of CO produced during FA decomposition has a significantly negative effect on LA hydrogenation over the supported platinum-group metals, although the possibility of formic acid as a poison on the LA hydrogenation cannot be completely ruled out.

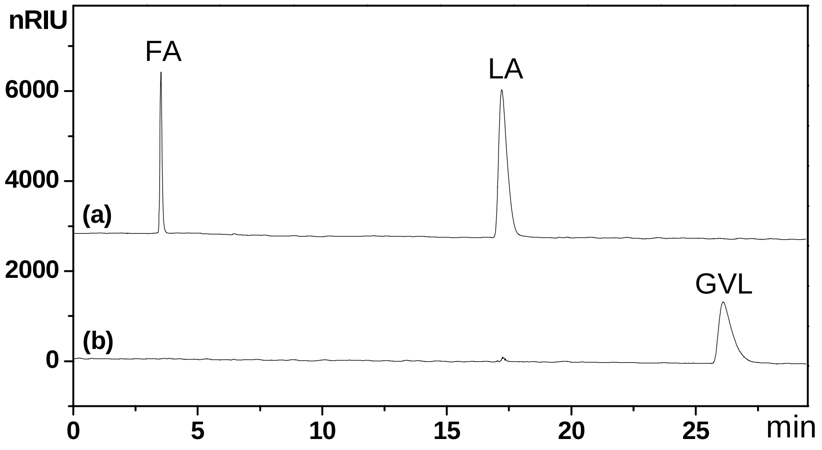


Fig S8. HPLC chromatograms of (a) the dehydration of fructose to LA and FA. Reaction conditions: fructose 10.8 g, 0.5 M H_2SO_4 (60 mL), 170 °C, 1h. (b) Reductive transformation of fructose-derived LA and FA using Au/ZrO_2-VS. Reaction conditions: the fructose-derived LA and FA (42 mL), Au (0.1 mol%), N_2 (0.5 MPa), 150 °C, 8 h (Table 2, entry 2).

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[S2] M. Haruta, *Catal. Today* **1997**, *36*, 153.

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[S7] L. Deng, Y. Zhao, J. Li, Y. Fu, B. Liao, Q. X. Guo, *ChemSusChem* **2010**, *3*, 1172.