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Supporting Information

A Versatile Aqueous Reduction of Bio-Based Carboxylic Acids using Syngas as a Hydrogen Source

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1. Materials and Methods

1.1 Catalytic materials

Levulinic acid (LA, 99 %), Itaconic acid (IA, 99.8 %), Succinic acid (99 %), Fumaric acid (99 %), Lactic acid (98 %), γ-valerolactone (GVL, 98 %) were supplied by Aladdin. Metal oxide SiO_2 (Evonik, Aerosil 380, specific surface area: 380 $m^2 \cdot g^{-1}$) was supplied from the Degussa. Palladium chloride ($PdCl_2$), rhodium chloride hydrate ($RhCl_3 \cdot xH_2O$), Ruthenium chloride hydrate ($RuCl_3 \cdot xH_2O$), chloroplatonic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) and chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$), were supplied by Aldrich and used without further purification. Gold catalysts including 0.8 wt% Au/C (type D, lot no. Au/C no. 38D) was supplied by the World Gold Council (WGC). 1 wt% Au/TiO_2 (Catalogue number 79-0165), was supplied by Mintek. 5 wt% Pd/C (stock # 38300) was supplied from Alfa Aesar.

1.2 Catalyst preparation

Preparation of biphasic zirconia (b-ZrO_2)

b-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). After 6 h stirring at room temperature, 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 115 m^2 g^{-1} (Micromeritics TriStar 3000).

Preparation of monoclinic zirconia (m-ZrO_2)

m-ZrO_2 powders were synthesized according to the literature procedure.[S2] Briefly, 7.40 g $ZrO(NO_3)_2 \cdot 2H_2O$ and 19.22 g $(NH_2)_2CO$ were dissolved in 80 mL deionized water at room temperature. After that, the solution was transferred into a Teflon-lined stainless-steel autoclave (100 mL) and maintained at 160 ^oC for 12h. The resulting precipitate was washed thoroughly with water and treated at 110 °C overnight in ambient air and then calcined at 400 ^oC for 4h in dry air. The BET surface area of the resultant material was 124 m^2 g^{-1} (Micromeritics TriStar 3000).

Preparation of tetragonal zirconia (t-ZrO_2)

t-ZrO_2 powders were synthesized according to the literature procedure.[S2] Briefly, 7.40 g $ZrO(NO_3)_2 \cdot 2H_2O$ and 19.22 g $(NH_2)_2CO$ were dissolved in 80 mL methanol at room temperature. After that, the solution was transferred into a Teflon-lined stainless-steel autoclave (100 mL) and maintained at 160 ^oC for 12h. The resulting precipitate was washed thoroughly with methanol and treated at 110 °C overnight in ambient air and then calcined at 400 ^oC for 4h in dry air. The BET surface area of the resultant material was 108 m^2 g^{-1} (Micromeritics TriStar 3000).

Preparation of Au/b-ZrO_2 catalysts:

Au/b-ZrO_2 catalysts were prepared by a modified deposition-precipitation (DP) method by mixing b-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 continuous stirring at 25 ^oC the catalyst was washed five times with deionized water and separated by filtration. The samples were dried at 110 ^oC in air for 1 h, followed by reduction with a stream of 5 vol% H_2/Ar at 300 ^oC for 2 h. The BET surface area of the resultant Au/b-ZrO_2 catalyst was 111 m^2 g^{-1}. The crystal phase of the final catalyst was composed of 56 % monoclinic phase and 44 % 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 1.0~2.5 nm in diameter (TEM in Figure S1). *Safety note:* The mixing of gold chloride and ammonia solutions may lead to the formation of explosive gold compounds (fulminating gold).[S3] Based on our experimental observations, mixing of ammonia solution (not concentrated, 0.25 M) with gold chloride solution with very low concentration (1 mM) at RT does not result in explosive and friction-sensitive gold compounds.

Preparation of Au/m-ZrO_2 catalysts

Au/m-ZrO_2 catalysts were prepared by a modified deposition-precipitation (DP) method by mixing m-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 300 ^oC for 2 h. The BET surface area of the resultant Au/m-ZrO_2 catalyst was 116 m^2 g^{-1}. The concentration of gold was 0.8 % Au by weight (ICP-AES).

Preparation of Au/t-ZrO_2 catalysts

Au/t-ZrO_2 catalysts were prepared by a modified deposition-precipitation (DP) method by mixing t-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 300 ^oC for 2 h. The BET surface area of the resultant Au/t-ZrO_2 catalyst was 105 m^2 g^{-1}. The concentration of gold was 0.8 % Au by weight (ICP-AES).

Preparation of Au/SiO_2 catalysts

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 300 ^oC for 2 h.

Preparation of Pd/m-ZrO_2, Pt/m-ZrO_2, Ru/m-ZrO_2, Rh/m-ZrO_2 catalysts

1 wt% Pd/m-ZrO_2, 1 wt% Pt/m-ZrO_2, 1 wt% Ru/m-ZrO_2 and 1 wt% Rh/m-ZrO_2 catalysts were prepared by incipient-wetness impregnation of the support, with aqueous solution of $PdCl_2$, $H_2PtCl_6 \cdot 6H_2O$, $RuCl_3$, $RhCl_3$ precursors of appropriate concentrations (typically 1.0 mL/g support). After a perfect mixing of the corresponding slurries, samples were dried under vacuum at room temperature for 12 h and then reduced in 5% H_2/Ar at 400 ^oC for 2 h.

1.3 Catalyst characterization

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. The detection limit for Au was 7 ppb.

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:[S4]

M % = $1.6 I_{M(\bar{1}11)}/[1.6 I_{M(\bar{1}11)} + I_{T(111)}]$, 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.

X-ray photoelectron spectroscopy (XPS): XPS data were recorded with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg Kα, hv = 1253.6 eV) was used. The C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BE).

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.

2. Catalytic activity measurements

2.1 General procedure for the reduction of LA into GVL

A mixture of LA (4.53 mmol), supported metal catalysts (metal 0.1 mol%), 2-methoxyethyl ether (2 mmol, internal standard), water (10 mL) were charged into a 50 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm under 4 MPa syngas 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.

2.2 Recovery and reuse of Au/m-ZrO_2

The reused catalyst was recovered by filtering the solid Au/m-ZrO_2 from liquid phase after reduction. The recovered catalyst was washed with acetone for three times and then with distilled water for several times. The catalyst was then dried under vacuum at room temperature for 12 h.

2.3 General procedure for the reduction of various bio-based carboxylic acids with syngas

A mixture of 10 mL 5 wt% aqueous solutions of bio-based carboxylic acids, Au/m-ZrO_2 catalysts, 2-methoxyethyl ether (2 mmol, internal standard) were charged into a 50 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm under 4 MPa syngas (H_2:CO=2:1) 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.

2.4 Procedure for kinetic experiments of the reduction of LA with syngas in the presence of a series of zirconia polymorphs supported gold catalysts

A mixture of LA (4.53 mmol), supported gold catalysts (Au 0.1 mol%), 2-methoxyethyl ether (2 mmol, internal standard), water (10 mL) were charged into a 50 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm at 120 °C under 4 MPa syngas (H_2:CO=2:1) for 30 min. 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 results are shown in Figure S4.

2.5 Procedure for kinetic experiments of liquid phase water gas shift reaction (LWGS)

A mixture of water (10 mL) and Au/m-ZrO_2 catalysts (112 mg) were charged into a 50 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm at 120 °C under 4 MPa CO for 60 min. The gas products were analyzed on a Agilent 6820 gas chromatograph equipped with a TDX-01 column and TCD detector. The results are shown in Scheme S1.

2.6 Procedure for kinetic experiments of the reduction of LA with H_2 and CO/H_2O, respectively

A mixture of LA (4.53 mmol), Au/m-ZrO_2 catalysts (Au 0.1 mol%), 2-methoxyethyl ether (2 mmol, internal standard), water (10 mL) were charged into a 50 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm at 120 °C under 4 MPa H_2 for 15 min or under 4 MPa CO for 30 min. 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 gas products were analyzed on a Agilent 6820 gas chromatograph equipped with a TDX-01 column and TCD detector. The results are shown in Scheme S1.

3. Results

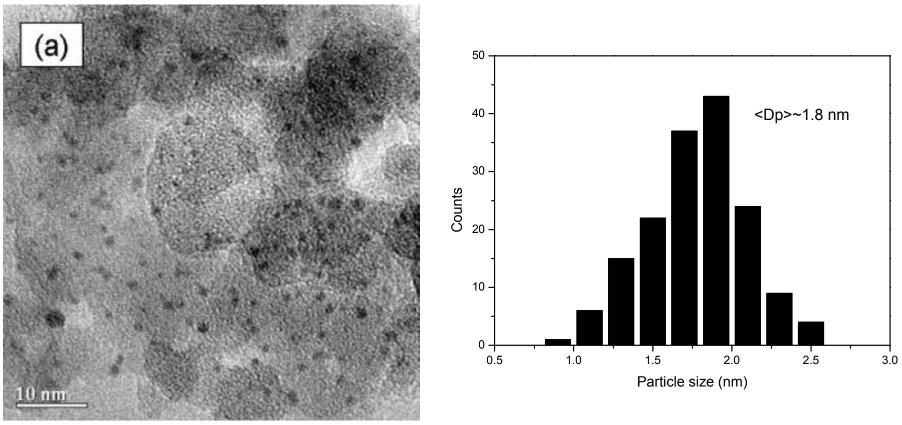
A. Reduction of various bio-based carboxylic acids using other noble metal catalysts

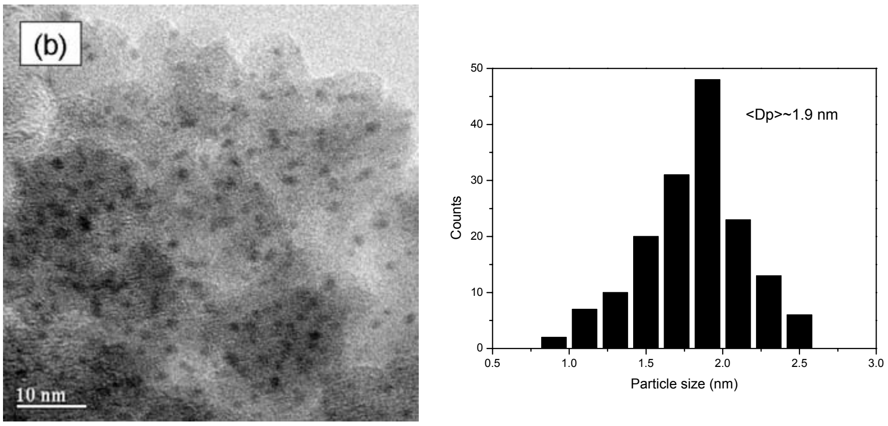
Table S1. Reductive transformation of various bio-based carboxylic acids into their corresponding lactones or diols with syngas catalyzed by different supported noble metal catalysts.[a]

Yield (%)[b]	Pt/m-ZrO_2	Pd/m-ZrO_2	Rh/m-ZrO_2	Ru/m-ZrO_2
Succinic acid	0	0	0	0
Fumaric acid[c]	0	0	0	0
Itaconic acid[d]	0	0	0	0
Lactic acid[e]	0	0	0	0

[a] Reaction conditions: 5 wt% aqueous solution of bio-based carboxylic acids (10 mL), metal (0.2 mol%), syngas (4 MPa, H_2:CO=2:1), 180 ^oC, 6h. [b] The yield was determined by GC using bis(2-methoxyethyl) ether as the internal standard. [c] 8h. [d] metal (0.1 mol%), 150 ^oC, 5h. [e] metal (1 mol%), 240 ^oC, 4h.

B. TEM analysis





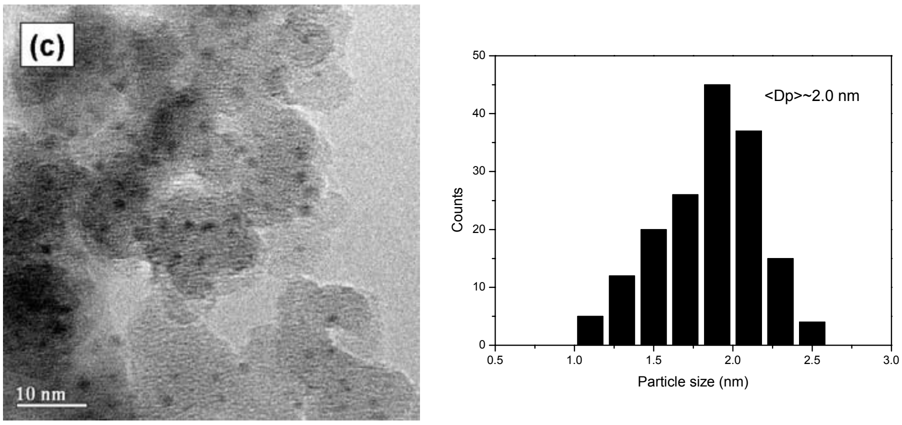


Figure S1. TEM image and gold particle size distribution of a) Au/b-ZrO_2; b) Au/m-ZrO_2; c) Au/t-ZrO_2.

C. XRD analysis

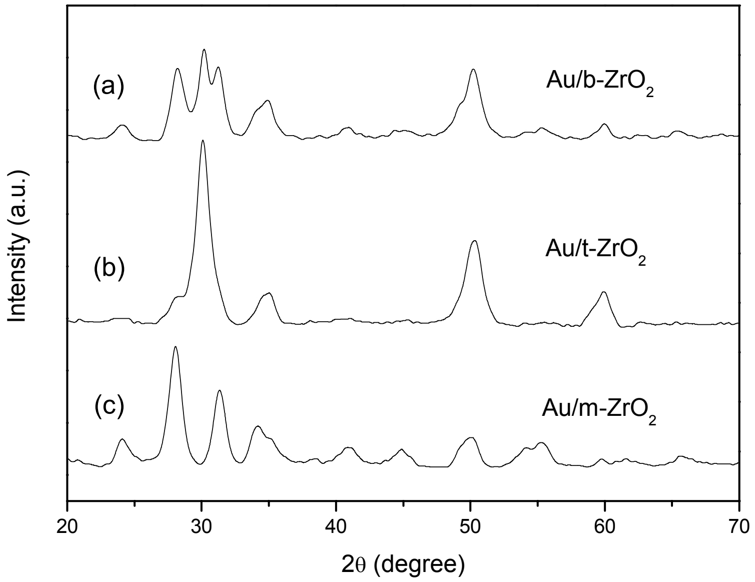


Figure S2. X-ray diffraction (XRD) patterns for a) Au/b-ZrO_2; b) Au/t-ZrO_2; c) Au/m-ZrO_2.

D. XPS analysis

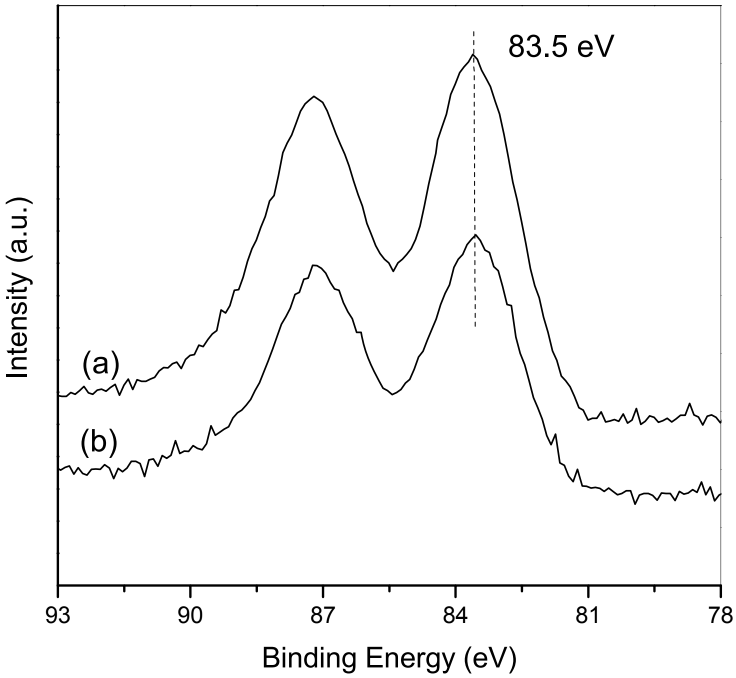


Figure S3. XPS for Au/m-ZrO_2 a) before reaction; b) after five runs. The binding energy of Au $4f_{7/2}$ for Au/m-ZrO_2 is ca. 83.5 eV. Note that the metallic state of Au practically undergoes no change after the five successive runs.

E. kinetic experiments of the reduction of LA with syngas in the presence of a series of zirconia polymorphs supported gold catalysts

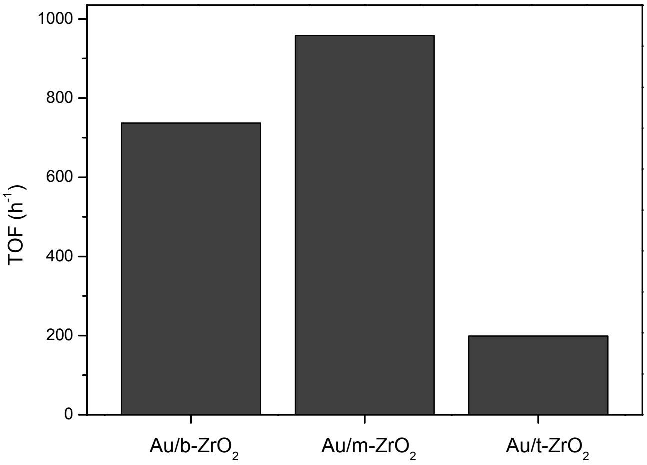


Figure S4. TOFs of gold catalyst supported on various ZrO_2 with different polymorphs. Reaction conditions: LA (4.53 mmol), Au (0.1 mol%), syngas (4MPa, H_2:CO=2:1), water (10 mL), 120 ^{o}C, 30 min.

F. Reaction profiles for LA reduction

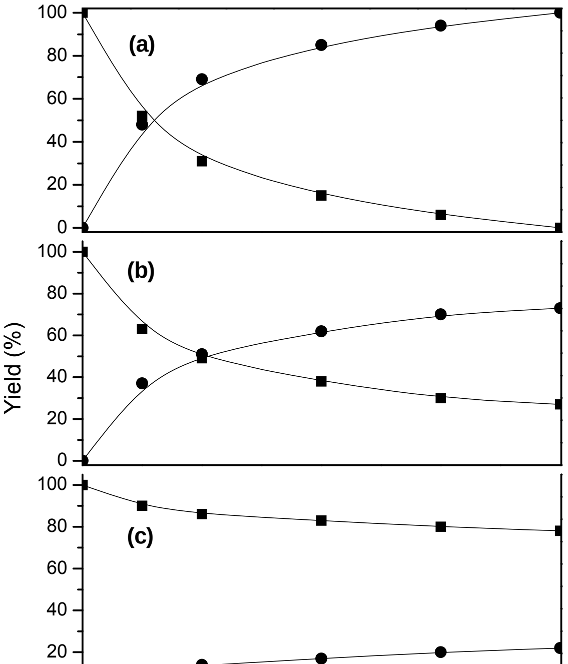


Figure S5. Time-course plot for LA reduction using syngas with (a) Au/m-ZrO_2, (b) Au/b-ZrO_2, (c) Au/t-ZrO_2 catalyst, respectively. Reaction conditions: LA (4.53 mmol), Au (0.1 mol%), syngas (4MPa, H_2:CO=2:1), water (10 mL), 120 ^oC. (●) GVL, (■) LA.

G. Kinetic experiments

Liquid phase water gas shift reaction (LWGS)

A mixture of water (10 mL) and Au/m-ZrO_2 catalysts (112 mg) were charged into a 50 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm at 120 °C under 4 MPa CO for 60 min to obtain a 2.9% CO conversion (Scheme S1a).

The reduction of LA with H_2

A mixture of LA (4.53 mmol), Au/m-ZrO_2 catalysts (Au 0.1 mol%), 2-methoxyethyl ether (2 mmol, internal standard), water (10 mL) were charged into a 50 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm at 120 °C under 4 MPa H_2 for 15 min to give GVL in 33% yield (Scheme S1b).

The reduction of LA with CO/H_2O

A mixture of LA (4.53 mmol), Au/m-ZrO_2 catalysts (Au 0.1 mol%), 2-methoxyethyl ether (2 mmol, internal standard), water (10 mL) were charged into a 50 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm at 120 °C under 4 MPa CO for 30 min to give GVL in 16% yield (Scheme S1c).

$$\text{(a)}\quad H_2O + CO \longrightarrow H_2 + CO_2 \qquad r_a=0.58\ \text{mmol}\ g_{Au}^{-1}\ s^{-1}$$

$$\text{(b)}\quad LA + H_2 \longrightarrow GVL \qquad r_b=1.86\ \text{mmol}\ g_{Au}^{-1}\ s^{-1}$$

$$\text{(c)}\quad LA + H_2O + CO \longrightarrow GVL \qquad r_c=0.45\ \text{mmol}\ g_{Au}^{-1}\ s^{-1}$$

Scheme S1. Initial reaction rates (r) calculated for the transformation catalyzed by 0.8% Au/m-ZrO_2 at 120 ^oC.

References

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