Conversion of Biomass-Derived Levulinate and Formate Esters into γ-Valerolactone over Supported Gold Catalysts

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The utilization of biomass has recently attracted tremendous attention as a potential alternative to petroleum for the production of liquid fuels and chemicals. We report an efficient alcohol-mediated reactive extraction strategy by which a hydrophobic mixture of butyl levulinate and formate esters, derived from cellulosic biomass, can be converted to valuable γ-valerolactone (GVL) by a simple supported gold catalyst system without need of an external hydrogen source. The essential role of the supported gold is to facilitate the rapid and selective decomposition of butyl formate to produce a hydrogen stream, which enables the highly effective reduction of butyl levulinate into GVL. This protocol simplifies the recovery and recycling of sulfuric acid, which is used for cellulose deconstruction.

Introduction

The conversion of renewable biomass to useful chemicals and fuels is one of the most important goals of green and sustainable chemistry.[1,2] Cellulose is the major component of plant biomass, which is readily available and does not compete with the food supply.[3,4] The challenge for the sustainable utilization of these natural resources is to develop cost-effective processing methods to transform highly functionalized carbohydrates into value-added chemicals and fuels.[5,6] In this respect, γ-valerolactone (GVL) has numerous properties that make it suitable as a promising new platform molecule for next-generation biorefineries.[7–9] In particular, it is considered to be a potential biofuel and unique feedstock that can be converted into liquid transportation fuels. Dumesic et al.[10] have developed an elegant integrated biorefinery process to convert GVL into hydrocarbon-based liquid fuels, which do not use external hydrogen or noble-metal catalysts. Alternatively, Lange et al.[11] have demonstrated that it is possible to produce a new family of fuels, known as valeric biofuels, by esterification of the pentenoic acid derived from GVL.

GVL can be obtained through the reduction of levulinic acid (LA, 4-oxopentanoic acid),[12] which is accessible from the acid hydrolysis of lignocellulosic biomass.[13] Indeed, LA preparation through hydrolysis with dilute sulfuric acid offers several key advantages over other techniques in terms of processing cost and scalability. An equimolar amount of formic acid (FA) is also produced during hydrolysis.[13,14] As a result, there is a growing interest in the use of FA as a viable and convenient sole source of hydrogen for LA reduction.[15–17] Although several promising strategies have been demonstrated to make GVL from LA and FA, these processes are plagued by the need to separate LA from H_2SO_4[18] as residual sulfur leads to the deactivation of the metal catalyst used for LA reduction or hydrogenation. To address the issue of H_2SO_4 management that is involved in GVL-centered biorefining, a new reactive extraction approach has been proposed to produce GVL though the intermediate formation of a hydrophobic mixture of levulinate and formate esters from biomass and olefins.[19] Despite its usefulness, this process suffers from some drawbacks, such as the inherently low formate ester decomposition rate and in particular the inconvenient need for external H_2 to facilitate the reduction kinetics.

Over the past few years, we have been interested in the unique catalytic properties of supported gold nanoparticles (NPs) and applied them to green, sustainable organic synthesis.[20] We have shown that small Au NPs (ca. 1.8 nm) deposited on zirconia (Au/ZrO$_2$) can successfully promote the effective, efficient conversion of aqueous biomass-derived LA and FA into GVL without using an external H_2 supply.[18] In continuation of our interest in the use of supported Au as sustainable catalysts for biomass transformations, we report an efficient alcohol-mediated reactive extraction protocol[21] that uses supported Au NPs as a robust and reusable catalyst to make GVL from biomass. As outlined in Scheme 1, our process relies on the extraction of LA and FA using hydrophobic alcohols (i.e., n-butanol), instead of alkenes,[19] for the intermediate production of levulinate and formate esters. Our results have shown that the simple Au/ZrO$_2$ system is highly efficient at making GVL from biomass-derived n-butyl levulinate (BL) and formate (BF) without external hydrogen gas. This process eliminates the need for costly neutralization steps and facilitates the separation and recycling of products.

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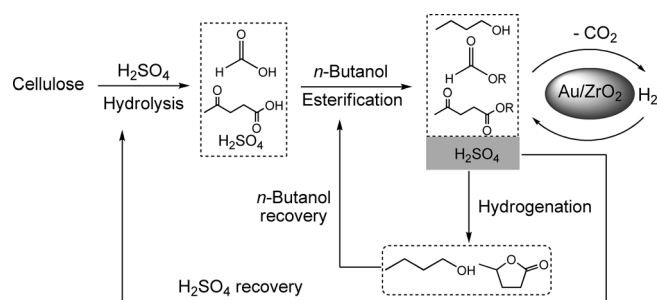
Scheme 1. The conversion of cellulose to GVL via BL and BF intermediates.

Results and Discussion

Esterification of LA and FA

We began our study by examining the alcohol-mediated esterification of an aqueous solution that contained equimolar concentrations of LA and FA, which is expected to represent the easiest model to simulate the proposed reactive extraction. The choice of *n*-butanol is based on the following: 1) to produce water-immiscible levulinate/formate esters, an alcohol with at least four carbon atoms is preferred;[21] 2) *n*-butanol is versatile, sustainable, and can be produced from a variety of waste biomass sources.[22] Table 1 shows the results for the re-

Table 1. Esterification of LA and FA with *n*-butanol under different aqueous phase concentrations, temperatures, and reaction times.[a]

Entry	LA [M]	FA [M]	T [°C]	t [h]	Yield[b] [%] BL	Yield[b] [%] BF	LA[c] [%] org.	LA[c] [%] aq.	FA[c] [%] org.	FA[c] [%] aq.
1	1	1	90	2	60	50	23	17	27	23
2	1	1	90	4	61	50	23	16	27	23
3	1	1	120	2	52	45	27	21	30	25
4	1	1	60	6	59	49	24	17	27	24
5	2	2	90	2	63	55	21	16	25	20
6	4	4	90	2	80	73	12	8	15	12
7	5	5	90	2	89	80	7	4	11	9
8	6	6	90	2	95	85	3	2	8	7

[a] Reaction conditions: butanol/(LA+FA) molar ratio is equal to 4:1. LA (10 mmol), FA (10 mmol), *n*-butanol (80 mmol), H_2SO_4 (2.5 mmol), solvent (water). [b] Selectivity of both BL and BF is 100%. [c] Partition coefficients (M_{org}/M_{aq}) of LA and FA are 1.4 and 1.2, respectively.

active extraction of LA and FA under various conditions. As shown in Entry 1, esterification of the aqueous solution that contained low concentrations (1 M) of LA and FA at 90 °C for 2 h only afforded the production of BL and BF in moderate yields. Extending the reaction time or varying the reaction temperature did not improve the yields of BL and BF (Table 1, Entries 2–4). Increasing the reaction temperature to 120 °C led to a substantial decrease in the yields of the ester products (Table 1, Entry 3), which may be because the reverse of the esterification, that is, the acid-catalyzed ester hydrolysis, is more favored at elevated temperatures.

A survey of other reaction parameters revealed that, under otherwise identical reaction conditions, the formation of BL

and BF esters can be greatly facilitated by the use of a concentrated solution of LA and FA (Table 1, Entries 5–8). This suggests that the concentration of the reaction medium is critical for the desired reaction pathway. Thus, under optimized conditions (Table 1, Entry 8), an excellent yield of over 95% was obtained for BL formation. A high yield (85%) of BF was also achieved in this case. After the esterification step, the aqueous phase, which contains H_2SO_4 and trace amounts of unconverted LA and FA, separated spontaneously from the organic products. These results are consistent with those of the butene-mediated reactive extraction established by Dumesic et al.[19] Such a separation was very useful as the aqueous phase that contains H_2SO_4 can be recycled for subsequent rounds of cellulose deconstruction, which eliminates an expensive, energy-consuming distillation step. The most significant finding, however, is that the organic phase in Entry 8 contains up to 98% of the LA and 93% of the FA that were present in the aqueous feed solution. The organic stream contained 98% of the LA initially present in the aqueous solution, 95% in the form of BL and 3% as unconverted LA. Analogously, the organic stream contained 93% of the FA initially present in the aqueous solution, 85% in the form of BF and 8% as unconverted FA.

Decomposition of BF

The above studies showed that an easily separable, hydrophobic mixture of levulinate and formate esters can be readily obtained by esterification of aqueous LA and FA with *n*-butanol catalyzed by dilute H_2SO_4 at 90 °C. Our subsequent studies focused on the production of hydrogen by BF decomposition over supported gold catalysts. Although formate esters, especially methyl formate (MF),[23] have long been known as an alternative source of syngas that can be applied to hydrogenation and hydrocarbonylation reactions, effective generation of CO/H$_2$ mixtures from anhydrous MF is extremely difficult and many reported procedures require the use of aqueous MF solutions that contain large amounts of water.[24] The essential role of water is attributed to its facilitation of a simple decarbonylation by its coupling with the water-gas-shift (WGS) reaction, which is based on results that show the enhanced production of H_2 and CO_2. To date, the most efficient catalyst reported for this reaction is a homogeneous $Ru_3(CO)_{12}$–phosphine complex, which only allows the conversion of aqueous MF into a mixture of H_2, CO, and CO_2 in moderate yields (ca. 49%) at 180 °C.[24] Therefore, the development of improved catalytic systems that can efficiently afford H_2/CO_2 from the decomposition of formate esters is still a matter of great interest.

The decomposition of BF was performed in a high pressure Parr reactor at 170 °C. Table 2 shows that the Au/ZrO_2 catalyst decomposed BF in water efficiently (Table 2, Entry 2). The decomposition of BF in the presence of Au/ZrO_2 gives H_2, CO_2, and *n*-butanol as the sole products. Compared to palladium, platinum, or ruthenium NPs (average particle size ca. 1–3 nm) supported on zirconia as reference catalysts, gold is far superior to other noble metals in terms of its performance for the effective and selective decomposition of BF (Table 2, Entries 3–5). Several activated-carbon-supported platinum-group-metal cat-

Table 2. Decomposition of BF over heterogeneous catalysts.[a]

Entry	Catalyst	t [h]	Conversion[c] [%]	H_2 yield [%]	Gas phase composition [%] H_2	CO_2	CO
1[b]	Au/ZrO$_2$	1	10	10	>49	>49	<1
2	Au/ZrO$_2$	1	100	100	50	50	0
3	Pt/ZrO$_2$	3	2	1.7	46	46	8
4	Ru/ZrO$_2$	3	5	4	44	44	12
5	Pd/ZrO$_2$	3	15	14	49	49	2
6	Pd/C	3	45	42	49	49	2
7	Ru/C	3	30	25	45	45	10
8	Au/TiO$_2$	1	60	60	50	50	0
9	Au/SiO$_2$	3	2	2	50	50	0
10	Au/C	3	3	3	50	50	0

[a] Reaction conditions: *n*-butyl formate (20 mmol), water (60 mmol), *n*-butanol (120 mmol), metal (0.1 mol%), $T = 170$ °C. [b] *n*-butyl formate (20 mmol), *n*-butanol (120 mmol), metal (0.1 mol%), $T = 170$ °C. [c] Determined by using GC with 2-methoxyethyl ether as the external standard.

Figure 2. Decomposition of ■) FA or ●) BF with Au/ZrO$_2$. Reaction conditions: reactant (20 mmol), Au (0.1 mol%), water (60 mmol), butanol (120 mmol), $T = 170$ °C, in a 25 mL Hastelloy-C high pressure Parr reactor.

alysts such as Ru/C and Pd/C were also evaluated, but they have very limited activities for this reaction (Entries 6 and 7). As the choice of the support plays an important role in gold catalysis, we also evaluated gold that was supported on TiO$_2$ (Au/TiO$_2$), which was prepared by a routine deposition–precipitation procedure.[20c] This catalyst only affords a 60% yield for the decomposition of BF (Table 2, Entry 8). In contrast, gold supported on silica (Au/SiO$_2$) and activated carbon (Au/C) are ineffective for the decomposition of BF under similar reaction conditions (Table 2, Entries 9 and 10). Except for that of Au/C, all of the above catalysts have similar mean metal-particle sizes of ca. 2 nm. Hence, it follows that both the noble metal and the nature of the support play a role in the catalytic activity of BF decomposition.

In analogy to previously reported homogeneous systems, the present heterogeneous Au-catalyzed formate ester decomposition may proceed through a decarbonylation and WGS sequence, particularly considering that supported gold has long been the catalyst of choice for WGS.[25]

An independent low temperature WGS did, however, not proceed completely under the experimental conditions employed in this work (Figure 1). In addition, control experiments
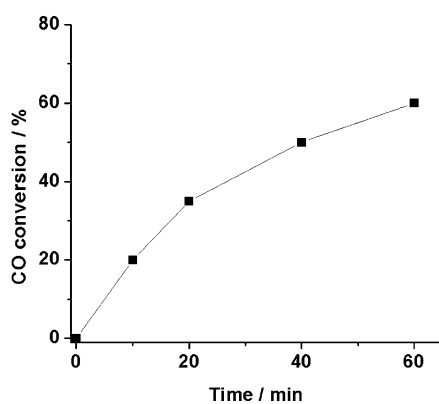
in the absence of water indicated that the sole decomposition of anhydrous BF over Au/ZrO$_2$ proceeded sluggishly, albeit with excellent selectivity to H_2/CO$_2$. Moreover, if FA was applied instead of BF, a significantly higher rate was observed for the Au-catalyzed FA dehydrogenation (Figure 2). Taken together, it can be seen that the gold-catalyzed BF decomposition does not involve a conventional WGS pathway, but a simple hydrolysis of the formate ester, which enables the decomposition to proceed through an FA intermediate.

Conversion of BL and BF into GVL

Having established that Au/ZrO$_2$ is able to catalyze the selective decomposition of BF at 170 °C, we looked to reduce BL to GVL using BF as the sole hydrogen source. The results in Table 3 show that it is possible to convert BL to GVL and *n*-butanol by consuming the hydrogen generated in situ by BF decomposition over the Au/ZrO$_2$ catalyst. It can be seen from Entry 1 in Table 3 that the conversion of a mixture of neat BL and BF proceeded smoothly at 170 °C. In line with the results of BF decomposition that are shown in Table 2, the rate of GVL formation can be increased significantly by the introduction of a suitable amount of water into the reaction system. A system-

Figure 1. WGS reaction with Au/ZrO$_2$ catalyst. Reaction conditions: CO (3.2 MPa at room temperature, equivalent to 20 mmol CO), Au (0.1 mol%), water (60 mmol), butanol (120 mmol), $T = 170$ °C.
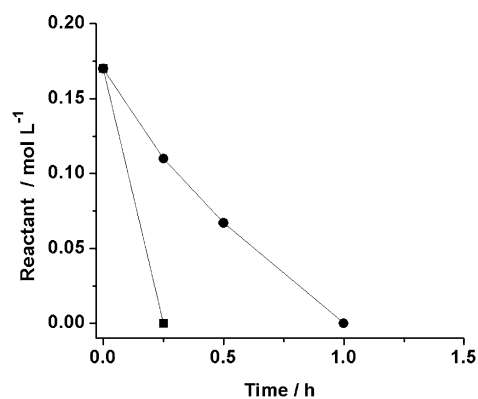
Table 3. Conversion of butyl levulinate and formate to GVL with Au/ZrO$_2$ catalysis.[a]

Entry	H_2O [mmol]	t [h]	Conversion[b] [%]	Yield[c] [%]
1	0	6	35	33
2	40	6	90	87
3	80	6	98	95
4[d]	80	6	96	94
5[e]	80	10	85	83
6[e]	80	15	96	94

[a] Reaction conditions: butyl levulinate (20 mmol), butyl formate (20 mmol), Au (0.1 mol%), $T = 170$ °C, N_2 (1 MPa). [b] Based on butyl levulinate. [c] Butyl 4-hydroxypentanoate was identified as an additional side product. [d] Results for the third run for the Au/ZrO$_2$ catalyst recycled under the reaction conditions described in Entry 3. [e] Butyl levulinate (20 mmol), butyl formate (20 mmol), Au (0.1 mol%), *n*-butanol (120 mmol), $T = 170$ °C, N_2 (1 MPa).
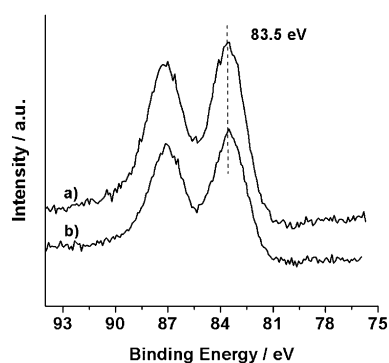
atic study on the effect of the molar ratio of water to BL or BF revealed that the reaction of BL/BF with 4 equiv. of water gave an optimal result (Table 3, Entry 3). Taking into account the prominent effect of water on the promotion of BL reduction with molecular H_2 (Figure 3), it is considered that the presence
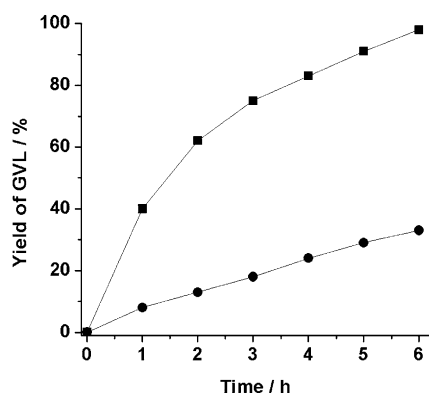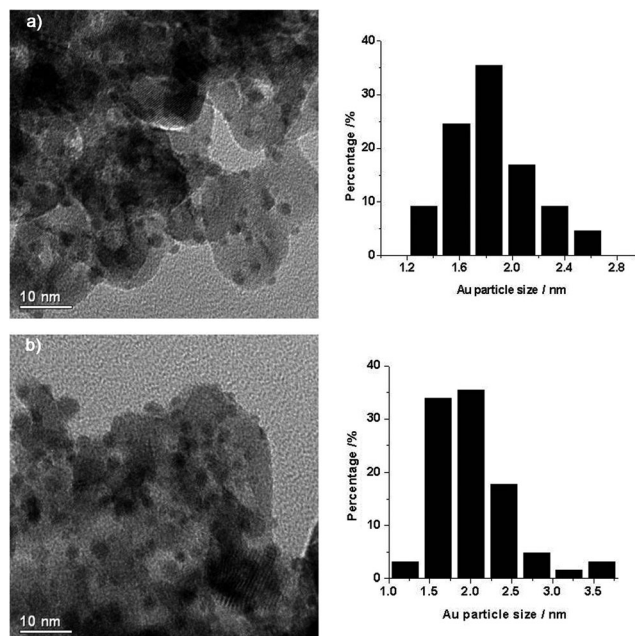

Figure 3. Conversion of BL to GVL with Au/ZrO$_2$. Reaction conditions: ■) BL (20 mmol), Au (0.1 mol%), water (40 mmol), H$_2$ (2.2 MPa at RT, equivalent to 20 mmol H$_2$), $T = 170\,°C$; ●) BL (20 mmol), Au (0.1 mol%), H$_2$ (2.2 MPa at RT, equivalent to 20 mmol H$_2$), $T = 170\,°C$, in a 25 mL Hastelloy-C high pressure Parr reactor.

Figure 5. TEM image and gold particle size distribution of a) fresh Au/ZrO$_2$ and b) Au/ZrO$_2$ after three runs; mean diameters of the Au NPs are ≈1.8 nm and ≈2.0 nm, respectively.

of water leads to the hydrolysis of butyl levulinate and formate, which enables the reduction to proceed through LA and FA intermediates and leads to a higher overall rate for GVL production. Under the conditions shown for Entry 3 in Table 3, near quantitative formation of GVL can be achieved after 6 h. The Au/ZrO$_2$ catalyst can be used at least three times, and retains a yield of GVL from BL of up to 94% (Table 3, Entry 4), which reflects the high stability and reusability of the catalyst. X-ray photoelectron spectroscopy (XPS, Figure 4) and TEM (Figure 5) showed no clear changes in the metallic state of Au and the mean diameter of the Au NPs, respectively, after three successive runs. Moreover, it was confirmed by induced coupled plasma techniques that the Au content of the used Au/ZrO$_2$ catalyst was the same as that of the fresh catalyst and there was no Au in the filtrate.

Given the high activity observed, more relevant studies have been performed to simulate the real feed produced from the

n-butanol-mediated reactive extraction process. To this end, we deliberately added an excess amount of *n*-butanol (10 mL) into the BL/BF mixture. One can see that GVL was still be obtained in up to 94% yield, although a longer reaction time was required (Table 3, Entries 5 and 6). Degradation products of *n*-butanol were not found under the conditions examined; see the Supporting Information for details. A high yield of GVL (ca. 95%) was also obtained from a hydrophobic mixture of butyl levulinate and formate esters that was derived from a reactive extraction of levulinic and formic acids with butene with a two-component Pd/C–Ru/C catalyst system.[19] In addition to the intrinsically low process productivity, this dual catalyst system required external H$_2$ gas (35 bar) to ensure that the desired reaction process proceeded. Thus, the most distinctive aspect of the Au/ZrO$_2$ catalyst system is that effective BL reduction was readily achieved with BF as the sole hydrogen source. Notably, the specific activity of BL conversion with Au/ZrO$_2$ is up to 64 mol h^{-1} mol$_{Au}^{-1}$ (corresponding to a BL conversion level of ≈96%), which is over ten times more active than the previously reported dual Ru/C–Pd/C catalytic systems.[19]

Production of GVL from cellulose

To demonstrate the utility of the alcohol-mediated reactive extraction protocol in the context of biorefining, we applied the method to the conversion of cellulose into GVL. First, we obtained a mixture of LA and FA from the acidic hydrolysis (catalyzed by 25 mL, 0.5 M H$_2$SO$_4$ at 150 °C for 5 h) of microcrystalline cellulose (2 g, 5% moisture, Sigma–Aldrich) with an average size of 20 μm. After a cycle of cellulose deconstruction, another batch of microcrystalline cellulose (2 g, 5% moisture) was added to the reaction mixture and the vessel was re-

Figure 4. XPS of Au/ZrO$_2$ a) before reaction and b) after three runs; the binding energy of Au 4f$_{7/2}$ for Au/ZrO$_2$ is ca. 83.5 eV.

sealed. This procedure was performed for five cycles.[26] After separation of the solid that remained at the end of the reaction, the aqueous solution contained 12 wt% LA and 5 wt% FA (the overall yields of LA and FA from cellulose are ca. 50%). Notably, without isolation of the insoluble hydrolysis by-products, the subsequent BL reduction was very slow under the reaction conditions described, which could owe to the strong adsorption of humins by the Au/ZrO$_2$ catalyst. The hydrolyzed solution was transferred into a 50 mL round-bottomed flask that contained n-butanol (0.2 mol) and subjected to a reaction at 90°C for 2 h. Analysis of the reaction mixture after the esterification step showed that the yields of BL and BF were 60 and 50%, respectively. Under these conditions, the organic stream also contains 5.8 mmol of unconverted LA and 6.8 mmol of unconverted FA. Thus, the organic phase contains 83% LA and 77% FA that were present in the aqueous feed solution initially. To this hydrophobic, organic stream were added the Au/ZrO$_2$ catalyst (0.1 mol%) and 4 equiv. of water, and the catalytic reduction of BL and LA using BF and FA as the in situ sources of hydrogen at 170°C produced GVL in 94% yield. The overall yield of GVL from cellulose was ca. 36%.

The yield of GVL was improved by concentrating the cellulose-derived LA and FA solutions. As shown in Scheme S1, the cellulose-derived LA (12 wt%) and FA (5 wt%) solutions were concentrated under reduced pressure using a rotary evaporator. Some of the water and FA were then removed (the boiling point of FA is close to water) by evaporation to obtain a more concentrated solution of LA (ca. 6 M), FA (ca. 3 M), and sulfuric acid. Subjection to reactive extraction with n-butanol at 90°C after 2 h led to the almost complete conversion of the mixture of LA and FA into a hydrophobic layer of BL and BF. The BL was converted into GVL using BF and FA (obtained from the evaporation step), as an in situ source of hydrogen, in the presence of Au/ZrO$_2$ (0.1 mol%). In this case, the overall yield of GVL from cellulose was 47%.

Conclusions

We have described a simple and efficient alcohol-mediated reactive extraction protocol for the production of γ-valerolactone (GVL) via butyl ester intermediates starting from cellulose, in which supported gold nanoparticles were facilitated the reduction of levulinic acid and its ester without using external hydrogen gas. This protocol simplifies the recovery and recycling of sulfuric acid for cellulose deconstruction, which allows for improved control of the overall process economics. The mixture of levulinic and formic esters, along with residual levulinic and formic acids, can be directly converted to an aqueous solution of GVL and n-butanol over a single Au/ZrO$_2$ catalyst, in which H$_2$, generated in situ from formic acid and its ester, is used for the reduction of levulinic acid and its ester to GVL. The operational simplicity and the improved efficiency of our new catalyst system are expected to contribute to its utilization for the cost-effective production of GVL or its derivatives from renewable lignocellulosic resources.

Experimental Section

Preparation of Au/ZrO$_2$ catalyst

Zirconia, with a Brunauer–Emmet–Teller (BET) surface area of 110 m^{2}g^{-1}, was prepared by a conventional precipitation method.[18] ZrOCl$_2$·8H$_2$O (12.9 g) was dissolved quickly in deionized water (200 mL) at room temperature and the pH adjusted to 9.0 by dropwise addition of NH$_4$OH (2.5 M). The resultant hydrogel was washed with deionized water until free of chloride ions. The precipitate was then dried at 110°C overnight and calcined at 400°C for 2 h in air. The Au/ZrO$_2$ catalyst was prepared by a modified deposition–precipitation method. ZrO$_2$ powder (2 g) was mixed with appropriate amounts of aqueous solutions of HAuCl$_4$ at room temperature. The pH was adjusted to 9.0 by the dropwise addition of 0.25 M NH$_4$OH. After 6 h of stirring at room temperature, the catalyst was washed with deionized water (5×100 mL) and separated by filtration. The samples were dried at 110°C in a forced air oven for 1 h and reduced with a stream of 5 vol% H$_2$/Ar at 350°C for 2 h. The BET surface area of the resultant Au/ZrO$_2$ catalyst (final mass ca. 1.9 g) was 113 m^{2}g^{-1}. The concentration of gold was 0.8 wt%, which was measured by inductively coupled plasma atomic emission spectroscopy. A large fraction of the Au particles in the catalyst was within 1.2–2.5 nm in diameter. XPS measurements showed that all the gold in the catalyst was in its metallic state.

Esterification of biomass-derived LA and FA

A mixture of LA (10 mmol), FA (10 mmol), n-butanol (80 mmol), H$_2$SO$_4$ (2.5 mmol), and water were charged to a 50 mL round-bottomed flask and stirred at a rate of 800 rpm under a 0.5 MPa N$_2$ atmosphere for the given reaction time (see Table 1). The mixture was heated to the desired temperature in less than 10 min. The organic liquid products BL and BF were analyzed by using a Shimadzu GC-17A gas chromatograph equipped with a capillary column HP-FFAP (30 m×0.25 mm) and FID detector. Aqueous samples were analyzed by using a HPLC (HP 1100, Agilent, USA) system with a Platisil ODS C18 column and a refractive index detector. H$_2$SO$_4$ (0.5 mM) was used as the mobile phase at a flow rate of 1 mLmin^{-1}. Both the column temperature and the detector temperature were 40°C.

Decomposition of BF

A mixture of BF (20 mmol), supported metal catalyst (metal 0.1 mol%), and water (60 mmol) were charged to a 25 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm under a 0.1 MPa He atmosphere for the given reaction time (see Table 2). The mixture was heated to 170°C in less than 15 min. After the reaction, the concentration of residual BF was analyzed by using a Shimadzu GC-17A gas chromatograph equipped with a capillary column HP-FFAP (30 m×0.25 mm) and FID detector (external standard: 2-methoxyethyl ether). The gaseous products were analyzed by using a GC analyzer equipped with a TDX-01 column and a thermal conductivity detector.

Conversion of BL and BF into GVL

A mixture of BF (20 mmol), BL (20 mmol), supported metal catalyst (metal 0.1 mol%), and water (80 mmol) were charged to a 25 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm under 0.1 MPa N$_2$ for the given reaction time. The mixture

was heated to 170 °C in less than 15 min. After the reaction, the concentration of residual BF was analyzed by using 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 use of GC–MS.

Recovery and reuse of Au/ZrO$_2$

The catalyst was recovered by filtration of the solid Au/ZrO$_2$ from the liquid phase after the reaction. The recovered catalyst was washed with acetone three times and then with distilled water several times. The catalyst was dried at 100 °C for 12 h. After three successive cycles, the catalytic activity of Au/ZrO$_2$ did not significantly decrease. Moreover, we did not detect the leaching of gold or ZrO$_2$ in the filtrate, which verifies the inherent stability of the Au/ZrO$_2$ catalyst during the reaction.

Production of GVL from cellulose

Microcrystalline cellulose (2 g, 5% moisture, Sigma–Aldrich) with an average size of 20 μm was loaded into a Teflon-lined stainless steel autoclave (100 mL) with 0.5 M H$_2$SO$_4$ (25 mL). The mixture was stirred vigorously at 150 °C under N$_2$ (0.5 MPa) for 6 h. After a cycle of cellulose deconstruction, another batch of microcrystalline cellulose (2 g, 5% moisture) was added to the reaction mixture and the vessel resealed. This procedure was performed for five cycles. After separation of insoluble humins produced during acid hydrolysis using a 0.2 μm cellulose acetate filter (Shanghai Bandao Chemical Co.), the liquid products were analyzed by using a HPLC (HP 1100, Agilent) system consisting of a Platisil ODS C18 column and a refractive index detector. H$_2$SO$_4$ (0.5 mM) was used as the mobile phase at a flow rate of 1 mL min^{-1}. Both the column temperature and the detector temperature were 40 °C. The hydrolyzed solution was transferred into a 50 mL round-bottomed flask containing *n*-butanol and refluxed at 90 °C for 2 h. The organic stream containing BL, BF and unconverted LA and FA separated spontaneously from the aqueous solution of H$_2$SO$_4$ after reaction. To the organic stream were added Au/ZrO$_2$ (0.1 mol%) and 4 equiv. of water. The catalytic reduction of BL and LA using BF and FA as an in situ source of hydrogen at 170 °C was then performed in a 25 mL Hastelloy-C high pressure Parr reactor.

To further improve the yield of GVL, the cellulosed-derived LA (12 wt%) and FA (5 wt%) solutions were concentrated under reduced pressure using a rotary evaporator. Some water and FA were then removed (the b.p. of FA is close to that of water) by evaporation to obtain a more concentrated solution of LA (ca. 6 M), FA (ca. 3 M), and H$_2$SO$_4$. The concentrated solution was transferred into a 50 mL round-bottomed flask with *n*-butanol and subjected to reflux at 90 °C for 2 h. The BL and BF separated spontaneously from the aqueous H$_2$SO$_4$ solution after the reaction. To the butyl esters were added Au/ZrO$_2$ catalyst (0.1 mol%) and FA solution (obtained from the evaporation step). Catalytic reduction of BL using BF and FA as an in situ source of hydrogen at 170 °C was then performed in a 25 mL Hastelloy-C high pressure Parr reactor (Scheme S1).

Acknowledgements

[1] A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Caimey, C. A. Eckert, W. J. Frederick Jr., J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* **2006**, *311*, 484–489.

[2] a) A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411–2502; b) M. J. Climent, A. Corma, S. Iborra, *Green Chem.* **2011**, *13*, 520–540.

[3] W. P. Deng, M. Liu, X. S. Tan, Q. H. Zhang, Y. Wang, *J. Catal.* **2010**, *271*, 22–32.

[4] a) A. Fukuoka, P. L. Dhepe, *Angew. Chem.* **2006**, *118*, 5285–5287. *Angew. Chem. Int. Ed.* **2006**, *45*, 5161–5163; b) N. Yan, C. Zhao, C. Luo, P. J. Dyson, H. C. Liu, Y. Kou, *J. Am. Chem. Soc.* **2006**, *128*, 8714–8715.

[5] J. J. Bozell, G. R. Petersen, *Green Chem.* **2010**, *12*, 539–554.

[6] A. L. Marshall, P. J. Alaimo, *Chem. Eur. J.* **2010**, *16*, 4970–4980.

[7] J. J. Bozell, L. Moens, D. C. Elliott, Y. Wang, G. G. Neuenscwander, S. W. Fitzpatrick, R. J. Bilski, J. L. Jarnefeld, *Resour. Conserv. Recycl.* **2000**, *28*, 227–239.

[8] H. Mehdi, V. Fábos, R. Tuba, A. Bodor, L. T. Mika, I. T. Horváth, *Top. Catal.* **2008**, *48*, 49–54.

[9] J. Q. Bond, D. M. Alonso, R. M. West, J. A. Dumesic, *Langmuir* **2010**, *26*, 16291–16298.

[10] J. Q. Bond, D. M. Alonso, D. Wang, R. M. West, J. A. Dumesic, *Science* **2010**, *327*, 1110–1114.

[11] J. P. Lange, R. Price. P. M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosselink, *Angew. Chem.* **2010**, *122*, 4581–4585; *Angew. Chem. Int. Ed.* **2010**, *49*, 4479–4483.

[12] L. E. Manzer, *Appl. Catal. A* **2004**, *272*, 249–256.

[13] S. W. Fitzpatrick, US Patent 5608105, **1997**.

[14] B. Girisuta, L. P. B. M. Janssen, H. J. Heeres, *Ind. Eng. Chem. Res.* **2007**, *46*, 1696–1708.

[15] R. J. Haan, J. P. Lange, US Patent 0208183, **2007**.

[16] a) L. Deng, J. Li, D. M. Lai, Y. Fu, Q. X. Guo, *Angew. Chem.* **2009**, *121*, 6651–6654; *Angew. Chem. Int. Ed.* **2009**, *48*, 6529–6532; b) L. Deng, Y. Zhao, J. Li, Y. Fu, B. Liao, Q. X. Guo, *ChemSusChem* **2010**, *3*, 1172–1175.

[17] H. Heeres, R. Handana, D. Chunai, C. B. Rasrendra, B. Girisuta, H. J. Heeres, *Green Chem.* **2009**, *11*, 1247–1255.

[18] X. L. Du, L. He, S. Zhao, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem.* **2011**, *123*, 7961–7965; *Angew. Chem. Int. Ed.* **2011**, *50*, 7815–7819.

[19] E. I. Gürbüz, D. M. Alonso, J. Q. Bond, J. A. Dumesic, *ChemSusChem* **2011**, *4*, 357–361.

[20] a) F. Z. Su, Y. M. Liu, L. C. Wang, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem.* **2008**, *120*, 340–343; *Angew. Chem. Int. Ed.* **2008**, *47*, 334–337; b) H. Sun, F. Z. Su, J. Ni, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem.* **2009**, *121*, 4454–4457; *Angew. Chem. Int. Ed.* **2009**, *48*, 4390–4393; c) L. He, L. C. Wang, H. Sun, J. Ni, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem.* **2009**, *121*, 9702–9705; *Angew. Chem. Int. Ed.* **2009**, *48*, 9538–9541.

[21] P. M. Ayoub, US 0047139 A1, **2006**.

[22] B. G. Harvey, H. A. Meylemans, *J. Chem. Technol. Biotechnol.* **2011**, *86*, 2–9.

[23] G. Jenner, *Appl. Catal. A-Gen.* **1995**, *121*, 25–44.

[24] G. Jenner, E. M. Nahmed, S. Libs-Konrath, *J. Mol. Catal. A-Chem.* **1991**, *64*, 337–347.

[25] J. Li, N. Ta, W. Song, E. S. Zhan, W. J. Shen, *Gold Bull.* **2009**, *42*, 48–60.

[26] J. C. Serrano-Ruiz, D. J. Braden, R. M. West, J. A. Dumesic, *Appl. Catal. B* **2010**, *100*, 184–189.