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

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Faced with the rapid depletion of natural resources and serious environmental issues, there is an ever-increasing demand for clean fuels and chemicals.[1] This reinforces a greater utilization of renewable resources to replace the conventional fossil-based feedstocks for chemicals and synthetic fuels.[2] Lignocellulose constitutes a major fraction of terrestrial biomass, which is readily available and does not compete with the food supply.[3] The challenge for the efficient utilization of these natural resources is to develop cost-effective processing methods to transform highly functionalized carbohydrates into value-added chemical structures, which is believed to be essential to build novel sustainable supply chains for the production of industrial chemicals.[4] In this respect, a potentially viable approach is the conversion of the carbohydrate fraction of lignocellulose into a set of defined platform molecules, which can serve as key intermediates or building blocks for the synthesis of a plethora of commodity and fine chemicals.[4b, 5] The implementation of such advanced biorefinery concepts requires the development of novel and versatile catalytic processes for the selective transformation of biomass-derived feedstocks to a broad range of valuable chemicals and materials.

Carboxylic acids are key platform chemicals for use as bio-based alternatives for fossil-fuel-based applications:[2b,c, 6] eight out of twelve platform chemicals identified by the US Department of Energy as top value-added chemical targets to produce from biomass are organic acids.[5a] These are used in the production of polymers, pharmaceuticals, solvents, and food additives, projecting an important market volume of carboxylic acids.[2b,c] The most common and straightforward approach for controlled and selective conversion of these renewable building blocks is through catalytic hydrogenations, which are often performed under highly agressive reaction conditions due to the low intrinsic reactivity of the carboxylic acid group with molecular hydrogen (H_2).[6f] Although a plethora of transition-metal-based systems capable of selective hydrogenation of

carboxylic acids have been reported,[6a–e] these reduction procedures rely mostly on a large-scale use of pure H_2. The H_2 produced today mainly comes from non-renewable fossil sources by very energy-intensive processes. From both economic and sustainable points of view, the development of new catalytic reduction processes that could substantially reduce the need for expensive H_2 gas would be of high interest.

Syngas, also known as synthesis gas, is a standard industry feedstock that comprises mainly a mixture of hydrogen and carbon monoxide (H_2/CO). As a key intermediate in the chemical industry, syngas is heavily used in a number of highly selective syntheses of a wide range of chemicals and fuels and also playing an increasing role in energy conversion.[7] Syngas can be produced from almost any carbonaceous sources ranging from natural gas and oil products to coal and biomass by oxidation with steam and oxygen.[7a–c] As a result, it represents a key for creating flexibility for the chemical industry and for the production of synthetic fuels (synfuels). The present use of syngas is primarily for the manufacture of ammonia and methanol, followed by the use of pure hydrogen for hydrotreating in refineries.[7a] Recent trends in the use of syngas are dominated by the conversion of inexpensive remote natural gas into liquid fuels (GTL) and by a possible role in a future "hydrogen economy" mainly associated with the use of fuel cells.[7a,d,e] Notwithstanding these versatile and broad applications, the direct use of syngas as a convenient and truly viable hydrogen source for valorization of bio-resources via catalytic reduction has not been reported.

The use of catalysts based on supported gold nanoparticles (NPs) or clusters for the processing and transformation of biomass into valuable chemicals is an area of growing interest.[8] Recently, from our continuing studies on heterogeneous gold catalysis,[9] we have discovered that small gold NPs (ca. 1.8 nm) deposited on a monoclinic/tetragonal biphasic zirconia (Au/b-ZrO_2) can deliver a facile hydrogen-independent conversion of aqueous levulinic acid (LA) and formic acid (FA) into γ-valerolactone (GVL),[10] a highly versatile intermediate that has attracted tremendous interest for preparing a range of valuable chemicals and liquid fuels from lignocellulosic biomass.[11] The essential role of supported gold is to facilitate rapid and selective decomposition of FA to produce a CO-free H_2 stream, thereby enabling a highly efficient reduction of LA without requiring an external source of H_2. Herein, we report that by using a single-phase monoclinic ZrO_2 supported gold catalyst, it is possible to realize a versatile aqueous reduction of a range of functionalized carboxylic acids to their corresponding lactones or diols utilizing syngas as a direct and economically more favored hydrogen source.

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In the first stage of our work, the conversion of LA using a H_2-rich syngas with H_2/CO ratio of 2, which is typical for methanol or Fischer–Tropsch synthesis,[7a,e,f] was chosen as a model to explore the feasibility of the proposed reaction. We initially examined the reduction of a diluted aqueous LA solution (0.45 M) at 120 °C in the presence of a series of zirconia polymorphs supported gold catalysts having a similar average gold particle size (ca. 2 nm). When using Au/b-ZrO_2, which has been reported as a very active and selective catalyst for FA-mediated LA conversion into GVL,[10] high conversion and selectivity were obtained with an initial turnover frequency (TOF) of 737 h^{-1} (see the Supporting Information) calculated from the initial reaction rate, as the number of GVL molecules formed per hour per gold atom. However, with the catalyst comprising gold NPs deposited on single-phase monoclinic zirconia (Au/m-ZrO_2), a much higher TOF (up to 958 h^{-1}) can be attained under identical reaction conditions. Importantly, the aqueous LA can be quantitatively converted to GVL over Au/m-ZrO_2 within 4 h (Table 1, entry 2). This result is remarkable, and becomes more relevant as the catalyst can be reused at least five times, while maintaining a 98% conversion and a yield up to 98% (Table 1, entry 3). Furthermore, it was confirmed by inductively coupled plasma atomic emission spectral (ICP-AES) analysis that there was no leaching of gold during the reaction, verifying the inherent stability of the Au/m-ZrO_2 catalyst.

To gain more detailed insight into the reaction performed with Au/m-ZrO_2, the time-course plot for the above mentioned

syngas-mediated LA reduction was examined (Figure S5). The reaction proceeded smoothly and was completed within 4 h. During the whole reaction process, GVL was the only product without detecting any other intermediates. Furthermore, in a series of additional studies examining the effect of pressure, it was revealed that the reaction time was greatly shortened from 6 to 3 h as P_{syngas} was increased from 2 to 5 MPa (Table 1, entries 2, 7–9). Subsequent experiments focused on the effect of the reaction temperatures revealed that under otherwise identical reaction conditions the Au/m-ZrO_2 catalyst exhibited rather low activity at 90 °C (Table 1, entry 5). Notably, at an elevated temperature of 150 °C, quantitative formation of GVL can be attained within 2 h (Table 1, entry 6). It should be stressed that, in this particular case the specific activity based on LA conversion is up to 2.54 $mol\,g_{Au}^{-1}\,h^{-1}$, which is over three times more active than the previously established FA-mediated Au/b-ZrO_2 catalytic systems.[10]

At this juncture, it is important to note that gold deposited on single-phase tetragonal ZrO_2 (Au/t-ZrO_2) can only afford a very moderate GVL yield (Table 1, entry 4), in line with the broad literature documenting the profound effect of polymorphic structure on the activity of ZrO_2-based catalysts.[12] The superior activity as found for Au/m-ZrO_2 with respect to Au/b-ZrO_2 and Au/t-ZrO_2 in this reaction could be due to a higher CO adsorption capacity as well as a higher abundance of hydroxyl groups of the Au/m-ZrO_2 catalyst.[12b] The high efficiency of Au/m-ZrO_2 for the direct reduction of LA using a H_2-rich syngas relative to other supported gold catalysts was shown clearly (Table 1). Au/TiO_2 and Au/SiO_2 resulted in poor yields, whereas Au/C did not promote the reduction at all (Table 1, entries 10–12). These results show that the combination of gold NPs with suitable polymorphs of ZrO_2 is essential for achieving a high catalytic activity for the selective reduction of LA into GVL using syngas under mild conditions. Moreover, we found that gold is uniquely active for LA reduction with syngas compared with other noble metals. The attempts to reduce LA to GVL with zirconia- or carbon-supported ruthenium, palladium, platinum, or rhodium NPs under the same reaction conditions were unsuccessful (Table 1, entries 13–17). These observations can be attributed to the intrinsically high affinity of ruthenium, palladium, platinum, and rhodium for CO adsorption,[13] which blocks their activity relative to gold.

Given the fact that the composition of syngas can vary quite significantly depending on the carbon source from which it is produced,[7a,b] we have explored the possibility to produce GVL via aqueous LA reduction using simulated syngas with varying H_2/CO feed ratio. To this end, three different volumetric compositions of syngas were examined in the Au/m-ZrO_2-mediated conversion of aqueous LA. As shown in entries 1–3 of Table 2, in all cases, LA can be quantitatively converted into GVL, albeit different reaction time is required. One interesting aspect that deserves special mention is that the reaction involving the H_2-rich syngas proceeds much more rapidly than with the CO-rich syngas. Of further interest is that inexpensive, renewable, and easily accessible CO_2-rich bio-syngas can also be successfully applied to the LA reduction (Table 2, entry 6). These results are extremely welcome in view of the fact that flexible and versa-

Table 1. Reductive transformation of aqueous LA into GVL with syngas in the presence of various catalysts.[a]
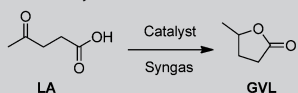
Entry	Catalyst	T [°C]	t [h]	P_{syngas} [MPa]	Conv.[b] [%]	Sel.[b] [%]
1	Au/b-ZrO_2	120	4	4	73	100
2	Au/m-ZrO_2	120	4	4	100	100
3[c]	Au/m-ZrO_2	120	4	4	98	100
4	Au/t-ZrO_2	120	4	4	22	100
5	Au/m-ZrO_2	90	4	4	24	100
6	Au/m-ZrO_2	150	2	4	100	100
7	Au/m-ZrO_2	120	3	5	100	100
8	Au/m-ZrO_2	120	5	3	100	100
9	Au/m-ZrO_2	120	6	2	100	100
10	Au/TiO_2	120	4	4	15	100
11	Au/SiO_2	120	4	4	3	100
12	Au/C	120	4	4	n.r.[d]	–
13	Pd/m-ZrO_2	120	4	4	n.r.[d]	–
14	Pt/m-ZrO_2	120	4	4	n.r.[d]	–
15	Ru/m-ZrO_2	120	4	4	n.r.[d]	–
16	Rh/m-ZrO_2	120	4	4	n.r.[d]	–
17	Pd/C	120	4	4	1	–

[a] Reaction conditions: LA (4.53 mmol), metal (0.1 mol%), simulated syngas ($H_2/CO = 2:1$), water (10 mL). [b] The conversion and selectivity were determined by means of GC using bis(2-methoxyethyl) ether as the internal standard. [c] Results for the fifth run with a recycled catalyst. [d] n.r. = no reaction.

Table 2. Effect of the syngas composition on aqueous LA reduction.[a]

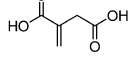| Entry	H_2/CO	P [MPa]	t [h]	Conv.[b] [%]	Sel.[b] [%]
1	2:1	4	4	100	100
2	1:1	4	5	100	100
3	1:2	4	6	100	100
4	pure H_2	4	2.5	100	100
5	pure CO	4	10	100	100
6	simulated bio-syngas[c]	4.4	4	100	100
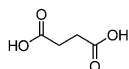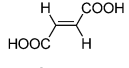
[a] Reaction conditions: LA (4.53 mmol), Au/m-ZrO$_2$ (Au 0.1 mol%), water (10 mL), 120 °C. [b] The conversion and selectivity was determined by means of GC using bis(2-methoxyethyl) ether as the internal standard. [c] H_2/CO = 2:1, CO/CO$_2$ = 5:1, CH$_4$/H$_2$ = 0.045:1; a typical simulated bio-syngas prepared in accordance with Reference [7f].

Table 3. Aqueous reductive transformation of various bio-based carboxylic acids with syngas in the presence of Au/m-ZrO$_2$.[a]

Entry	Carboxylic acids	T [°C]	t [h]	Conv.[b] [%]	Product	Sel.[b] [%]
1[c]	succinic acid	180	6	100	γ-butyrolactone	>99
2[c]	fumaric acid	180	8	100	γ-butyrolactone	>99
3	itaconic acid	150	5	100	3-methyl-γ-butyrolactone	92
4[d]	lactic acid	240	4	100	1,2-propanediol	87

[a] Reaction conditions: 5 wt% bio-based carboxylic acid (10 mL), Au/m-ZrO$_2$ (Au 0.1 mol%), syngas (4 MPa, H_2/CO = 2:1). [b] The conversion and selectivity was determined by means of GC using bis(2-methoxyethyl) ether as the internal standard. [c] Au (0.2 mol%). [d] Au (1 mol%).

tile syngas can be used as a direct and viable hydrogen source for selective biomass conversion, which may open the possibility to develop novel cost-effective technologies for the production of industrial chemicals based on platform molecules.

To better understand the essential role of H_2 and CO in the present syngas-mediated LA reduction, two independent experiments using pure H_2 and CO/H_2O as the hydrogen source were carried out. Under identical conditions the reaction can proceed to completion within 2.5 h when using H_2 as the sole reductant (Table 2, entry 4), in sharp contrast to the case with pure CO as the reductant (Table 2, entry 5). A careful analysis of the kinetic data allows us to estimate that the reduction rate of LA using H_2 (1.86 mmol g$_{Au}^{-1}$ s^{-1}) is around four times faster than that using CO/H_2O (0.45 mmol g$_{Au}^{-1}$ s^{-1}). This accounts for the significantly slower reduction rate associated with the CO-rich syngas atmosphere.[14] To gain deeper insight into the reaction pathways involved in the CO/H_2O-mediated LA reduction, we performed an additional parallel experiment to monitor the reaction kinetics of liquid phase water gas shift reaction (LWGS, CO + H_2O ⇌ H_2 + CO$_2$) in the absence of LA (see Supporting Information). The rate of H_2 formation via LWGS (0.58 mmol g$_{Au}^{-1}$ s^{-1}) in the presence of Au/m-ZrO$_2$ is comparable to that of the pure CO-mediated GVL generation (0.45 mmol g$_{Au}^{-1}$ s^{-1}).[15] This indicates that crucial H_2 generation by LWGS is the kinetically relevant step in the overall reaction when using sole CO/H_2O as the hydrogen source.

Building upon these results, we started to extend this new gold-catalyzed syngas-mediated aqueous hydrogenation protocol to a wider range of bio-derived carboxylic acids. The results are summarized in Table 3. The reaction proceeds successfully with a number of fermentation-derived C$_4$- and C$_5$-dicarboxylic acids. For example, succinic and fumaric acids can be selectively hydrogenated to γ-butyrolactone (GBL),[16] a valuable chemical intermediate widely used as solvent as well as in the production of plastics and polymers,[2b,c,17] in high yields (Table 3, entries 1 and 2). In addition, the catalyst system can be readily adapted to itaconic acid (IA), an unsaturated dicarboxylic acid with interesting commercial possibilities.[2b,c] In the only related precedent to this work a bifunctional ruthenium complex bearing specifically designed phosphine ligands was used as a hydrogenation catalyst for the conversion of IA

under H_2 atmosphere, whereby a 1.2:1 mixture of the two regioisomers of methyl-γ-butyrolactones (3-MGBL and 2-MGBL) was obtained in a combined yield of about 80%.[6b] Remarkably, the hydrogenation of IA over Au/m-ZrO$_2$ is highly regioselective, producing 3-MGBL in excellent yield of up to 92% (Table 3, entry 3).

Furthermore, the catalyst system also shows promise for highly selective reduction of lactic acid, the most important hydroxycarboxylic acid that can be derived from biological fermentation.[2b,c,6a,18] The more challenging reduction of the carboxylic-acid function in this molecule as compared to LA was reflected in a much higher reaction temperature required for the conversion of lactic acid. In contrast to the situation for the selective transformation of the C$_4$- and C$_5$-dicarboxylic acids described above, wherein the formation of corresponding lactones was frequently found to proceed through a dual-step hydrogenation/dehydration sequence, the present Au/m-ZrO$_2$-syngas system can deliver a selective reduction of the carboxylic acid function in lactic acid, thus offering a renewable-based pathway to 1,2-propanediol,[19] a high demand commodity chemical currently manufactured by the oxidation of petroleum-derived propylene.[18] Again, it is important to note that neither the Pt, Pd, Rh nor Ru catalysts were active for the above reactions (see Table S1), which further confirms the indispensable role of Au in mediating the relevant reduction process using syngas as a direct hydrogen source.

In summary, the results of the present study demonstrate that zirconia-supported gold catalysts and in particular the Au/m-ZrO$_2$ system show a very promising potential for the selective reduction of bio-derived platform chemicals using readily available syngas as a convenient and cost-competitive hydrogen source. To the best of our knowledge, this new Au-based catalytic protocol constitutes the first biomass valorization system directly using versatile and flexible syngas as a viable hydrogen source and furnishes a new application of syngas apart from conventional fuel production and chemical synthe-

sis. As the controlled hydrogenation or reductive transformation is a very general issue in the conversion of bio-derived substrates, the procedure described herein is expected to be of broad applicability in the utilization of biomass.

Experimental Section

Preparation of Au/m-ZrO$_2$ catalysts: Monoclinic zirconia (m-ZrO$_2$) was synthesized according to the literature procedure.[12a] Au/m-ZrO$_2$ catalysts were prepared by a modified deposition–precipitation (DP) method by mixing as-synthesized *m*-ZrO$_2$ powders (2 g) with suitable 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$_4$OH. After 6 h continuous stirring at room temperature the catalyst was washed five times with deionized water and separated by filtration. The samples were dried at 110 °C in a forced air oven for 1 h, followed by reduction with a stream of 5 vol % H$_2$/Ar at 300 °C for 2 h. Elemental analysis results revealed that the real gold loading was 0.8 wt % in Au/m-ZrO$_2$.

Safety note: The mixing of gold chloride and ammonia solutions may lead to the formation of explosive gold compounds (fulminating gold).[20] 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 room temperature does not result in explosive and friction-sensitive gold compounds.

General procedure for the reduction of LA: 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 a given reaction time. The mixture of substrates and catalyst was heated to the desired temperature in less than 15 min. The liquid products were analyzed by using a Shimadzu GC-17A gas chromatograph equipped with a capillary column HP-FFAP (30 m×0.25 mm) and flame ionization detector. The identification of the products was performed by using a GC–MS spectrometer.

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[15] The presence of carboxylic acids may significantly depress the LWGS reaction under otherwise identical conditions. This possibility is confirmed by the fact that the rate of H$_2$ formation via LWGS decreased from 0.58 to 0.32 mmol g$_{Au}^{-1}$ s^{-1} when 4.53 mmol butyric acid was deliberately added.

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