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Conversion of Carbohydrate Biomass to γ-Valerolactone by using Water-Soluble and Reusable Iridium Complexes in Acidic Aqueous Media

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Diminishing fossil fuel reserves and degradation of the environment are strong driving forces for developing an efficient process to convert renewable feedstocks into liquid fuels and valuable chemicals. Biomass provides an abundant and renewable alternative to fossil resources for the sustainable production of energy and chemicals.[1] The largest part of woody biomass is carbohydrates, which is, therefore, of particular interest for conversion into platform molecules that can be utilized to produce liquid fuels, feedstock chemicals, and fine chemicals.[2] Because of its versatile functions and benign properties, γ-valerolactone (GVL) is considered one of the most promising reproducible platform molecules.[3] GVL can be converted into transport fuels, fuel additives,[4] solvents,[5] food additives, perfumes, and organic intermediates for the production of fine chemicals.[6] In this respect, recent efforts have been focused on the development of ecofriendly, efficient, and inexpensive processes for the synthesis of GVL. One of the most effective methods that can be used for the manufacture of GVL is the hydrogenation of levulinic acid (LA), which can be obtained through the hydrolysis of carbohydrate biomass.[7] LA can be converted into GVL with molecular hydrogen or formic acid (FA) with either heterogeneous[8] or homogeneous catalysts.[9]

Typically, heterogeneous catalysis facilitates the separation and recycling processes, but the catalytic efficiency is relatively low and high temperatures, high pressure, or a combination of both are required to ensure satisfactory conversions and yields. In contrast, homogeneous catalyst has high catalytic efficiency with the turnover numbers (*TON*s), that is, moles of substrate per mole of catalyst, of up to 71 000.[9i] However, in addition to the inherent limitations of the homogeneous catalytic processes, it requires strict absence of water and an additional excess of alkali to improve the reduction kinetics and minimize deactivation. Considering that the biomass hydrolysis process has a rich water content and extremely high acidity, there may be serious shortcomings in the energy consumption and processing costs, as well as additional handling problems. To minimize the cost of the GVL feed, two key problems regarding GVL production need to be resolved.[8d] First, LA should be obtained from carbohydrate biomass feeds through a simple and robust hydrolysis process. Secondly, for compatibility with the hydrolysis step, low concentrations of LA formed in acidic aqueous medium should be reduced to GVL without separation, evaporation, or pH adjustment by using a highly efficient catalyst. Therefore, the development of a highly efficient catalytic system, which can be reused in strongly acidic aqueous solution, for the reduction of LA derived from carbohydrate biomass is particularly important.

Himeda et al.[10] and Ogo et al.[11] reportedly used a series of half-sandwich iridium complexes for hydrogenating carbon dioxide with high *TON*s in aqueous media. Hence, we deduced that robust iridium complexes could be efficient catalysts for the hydrogenation of biomass-derived LA in water. Herein, we show that half-sandwich iridium complexes serve as highly efficient and robust homogeneous catalysts for the generation of GVL from various biomass-derived carbohydrates (i.e., cellulose, starch, and sugars). More importantly, this water-soluble homogeneous catalyst can be reused by applying a simple phase separation for the selective reduction of low concentration LA with molecular hydrogen or FA in aqueous solution without any additives.

We initially investigated the influence of the electronic and steric hindrance effects of the substituents on the yields. The initial experiments were performed at 1.01 MPa H_2 and 120 °C in water in the presence of 0.01 mol % of the half-sandwich iridium catalyst (Scheme 1 and Table 1). After 4 h, for catalyst **1** without any substituent group, we observed that the GVL yield was 31 %. When a single carboxyl group was substituted at the *meta*-position (catalyst **2**), the yield decreased to 11 %, and with double carboxyl group substitution (catalysts **3** and **4**), the yield was even lower. This could be because the catalytic efficiency of this reaction is closely related to the ligand σ-donor power of the substituent on the bipyridine ligand backbone. Clearly, the electron-withdrawing groups weaken the activity of the catalyst. Next, we replaced the carboxyl group with hydroxyl functionality (catalyst **5**) and obtained a 96 % yield of GVL. When we used stronger electron-donating substituents, such as a methoxy group (catalyst **6**), we obtained the highest GVL yield of 98 %. Steric hindrance was another factor that influenced the catalytic efficiency, which explained the reduced activity of catalyst **7**. The yield reduced significantly for catalyst **8**, which was likely caused by dehydrogenation.[12] To validate this speculation, we used GVL as a raw material with catalyst **8** under identical conditions, and we received a 71 % recovery of GVL and observed that LA was formed during the reaction process. Interestingly, the activity

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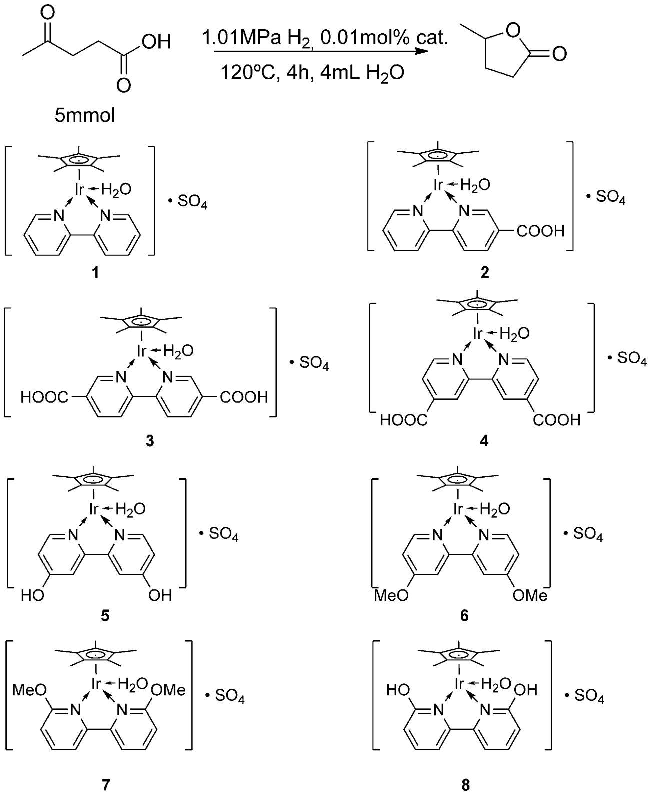


Scheme 1. The hydrogenation of LA and the structures of the different iridium complexes used. (Reaction conditions: 5 mmol LA, 1.0 mL 0.5 mmol L^{-1} aqueous solution of catalyst (i.e., 0.01 mol% cat.), 4.0 mL H_2O, 1.01 MPa H_2 (initial), 120 °C, 4 h.

Table 1. Catalytic reduction of LA to GVL.[a]

Entry	Catalyst	Cat. loading [mol%][b]	Reductant	Yield [%][c]
1	**1**	0.01	1.01 MPa H_2	31
2	**2**	0.01	1.01 MPa H_2	11
3	**3**	0.01	1.01 MPa H_2	2.1
4	**4**	0.01	1.01 MPa H_2	1.9
5	**5**	0.01	1.01 MPa H_2	96
6	**6**	0.01	1.01 MPa H_2	98
7	**7**	0.01	1.01 MPa H_2	77
8	**8**	0.01	1.01 MPa H_2	21
9[d]	**6**	0.001	1.01 MPa H_2	78
10	**6**	0.01	2.0 equiv. FA[b]	99
11	**6**	0.01	1.5 equiv. FA[b]	85
12	**6**	0.01	1.2 equiv. FA[b]	71
13[e]	**6**	0.01	1.2 equiv. FA[b]	76
14[f]	**6**	0.1	2.0 equiv. FA[b]	94

[a] Reaction conditions: LA (5 mmol), aqueous solution of catalyst (1.0 mL), H_2O (4.0 mL), 120 °C, 4 h. [b] Catalyst loading and amount of FA based on the amount of LA. [c] Calculated by using GC (all selectivities were over 99%). [d] 36 h. [e] 6 h. [f] 25 °C, 24 h.

of catalyst **6** was high even when the catalyst loading was reduced from 0.01 to 0.001 mol%; after 36 h we still obtained a 78% GVL yield under 1.01 MPa H_2. To our best knowledge, this is the highest *TON* (78000) reported under mild reaction conditions for the hydrogenation of LA. Another crucial property regarding the economic potential of the catalyst system is the turnover frequency (TOF), and it is also important to note that the TOF of catalyst **6** is the highest reported to date (see Table S1 in the Supporting Information).

It has been reported that half-sandwich iridium-complex catalysts could be used to convert FA into hydrogen with highly efficiency.[13] Also, FA is a byproduct that is formed in an equimolar amount with LA from the acidic hydrolysis of biomass. From an economic and engineering perspective, we used FA as an in situ source of hydrogen instead of using hydrogen gas itself. Under otherwise identical conditions, the yield of GVL from 1:2 (molar ratio) aqueous mixtures of LA and FA was more than 99%. When the ratio was changed to 1:1.5, the yield reduced to 85%, and with a ratio of 1:1.2, the yield reduced to 71%. Even when we prolonged the reaction time to 6 h, the yield only increased slightly to 76%. These results indicated that excess FA was required in our reaction system, or that we needed to add external hydrogen to enhance the activity of the catalyst. Interestingly, when we simply increased the catalyst loading from 0.01 to 0.1 mol%, the catalyst showed excellent activity at room temperature, and after 24 h we obtained a GVL yield as high as 94%. To the best of our knowledge, this represents the mildest reaction conditions to achieve such a high yield in water with FA (Table S2, the Supporting Information).

To test the reusability and the stability of catalyst **6**, we again conducted the LA conversion reaction under identical conditions (Figure 1). After the reaction, GVL was extracted by using ethyl ether or methyl *tert*-butyl ether, and separated from the catalyst before it was reused in the next run. The yield of GVL remained at 94% after 5 runs, which proved that the catalytic activity did not decrease in this reaction system. Therefore, the catalyst could be reused, which is crucial for practical applications.

According to previous reports, the Ir–H species could be formed as an active catalytic intermediate during the reaction process.[14] To investigate the stability of iridium complexes in strong acidic solution, we used 4.0 mL of 0.5 mol L^{-1} H_2SO_4 aqueous solution instead of water, with all other conditions unchanged; the catalytic efficiency was not affected. Based on this result, we predicted that half-sandwich iridium complexes could be applied in the acidic hydrolysis of biomass. We tested several types of sugars to study the catalytic performance of catalyst **6** (Table 2). First, we obtained an acidic aqueous solution, which contained LA and FA, through the hydrolysis of glucose (0.9 g in a 5 mL aqueous solution, catalyzed by 0.5 mol L^{-1} H_2SO_4 at 170 °C with 0.5 MPa N_2). We then removed any insoluble solid out of the mixture through filtration. The filtered mixture was transferred into an autoclave containing catalyst **6** (0.01 mol%) and 1.01 MPa H_2. GVL was generated in 97% yield based on the conversion of LA after 4 h at 120 °C, and the overall GVL yield was 45%. Therefore, we demonstrated the high efficiency of catalyst **6** for the conversion of glucose to GVL. When we used fructose instead of glucose, we obtained an overall yield of 61%, which was the highest among all of the carbohydrate biomass sources that we tested. In addition to these monomeric C_6 sugars, we tested the activity of catalyst **6** for the conversion of sucrose, starch, and cellu-

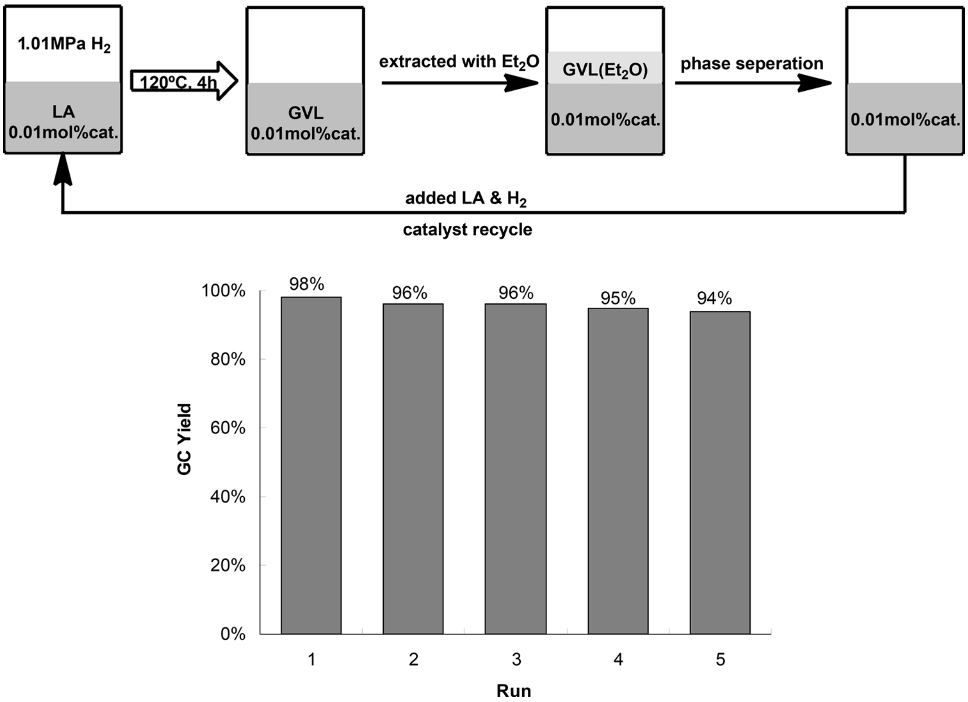
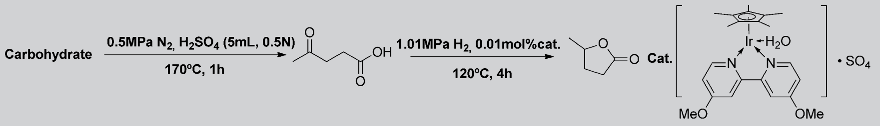


Figure 1. Reuse of catalyst **6** for the hydrogenation of LA in aqueous solution after a phase separation to recycle the catalyst. The organic phase (light grey) contained the product and the aqueous phase (dark grey) contained the catalyst.

Table 2. Dehydration of carbohydrates[a] and the subsequent reduction of carbohydrate-derived LA in the presence of catalyst **6**.[b]



Entry	Carbohydrate	FA yield [mol %][c]	LA yield [mol %][c]	GVL yield [mol %][d]
1	glucose	51	46	45 (97)
2	fructose	68	62	61 (98)
3	sucrose	58	53	52 (99)
4	starch	52	46	42 (92)
5	cellulose	43	37	34 (92)

[a] Reaction conditions: carbohydrate (0.9 g), H_2SO_4 aqueous solution (0.5 mol L^{-1}, 5 mL), N_2 (0.5 MPa), 170 °C, 1 h. [b] Reaction conditions: filtrate from hydrolysis (4 mL), aqueous solution of catalyst **6** (0.5 mmol L^{-1}, 1 mL), H_2 (1.0 MPa), 120 °C, 4 h. [c] Yield for the initial carbohydrate hydrolysis, consistent with reference [6b]. [d] Overall yield for the two-stage conversion of the biomass-derived carbohydrate. The yield based on the conversion of LA is shown in parenthesis.

lose. For sucrose, we observed near-complete conversion of LA to GVL. The yield of GVL from LA was also very high in the starch and cellulose experiments. For the conversion of carbohydrate biomass to GVL we obtained an overall yield of 52%, 42%, and 34% for sucrose, starch, and cellulose, respectively. These results demonstrated that catalyst **6** could be used for the generation of GVL from carbohydrate biomass resources with the addition of hydrogen, without the need for any separation or pH adjustment.

In summary, we report that half-sandwich iridium complexes can be used to convert LA into GVL in excellent yields under mild temperatures and pressures. We observe *TON*s up to 78,000 at 120 °C and 1.01 MPa H_2, which is the highest *TON* reported to date. The catalyst also shows high activity for the generation of GVL from aqueous mixtures of LA and FA, when excess FA or extra hydrogen is supplied, under the mildest conditions reported so far. Furthermore, through a simple phase separation, this water-soluble homogeneous catalyst can be reused for the selective reduction of low-concentration LA in aqueous solutions. Therefore, this catalyst can be used for the generation of GVL from various biomass-derived carbohydrates, indicating its superiority in practical applications for the industrial production of GVL.

Experimental Section

LA (99%), FA (98%), and GVL (98%) were purchased from Aladdin Reagent Co. Ltd. (Pentamethylcyclopentadienyl) iridium(III) chloride dimer [$(Cp^*IrCl_2)_2$, 98%] was purchased from Suzhou Sinocompound Technology Co., Ltd. Silver sulfate was purchased from Sinopharm Chemical Reagent Co. Ltd. Fructose (99%), glucose (99%), sucrose (99%), starch (soluble), and cellulose (microcrystalline) were purchased from Alfa Aesar. 2,2′-bipyridine, 4,4′-dicarboxy-2,2′-bipyridine, 5,5′-dicarboxy-2,2′-bipyridine, and 4,4′-dimethoxy-2,2′-bipyridine were purchased from TCI. 5-carboxy-2,2′-bipyridine,[15] 4,4′-dihydroxy-2,2′-bipyridine,[16] 6,6′-dihydroxyl-2,2′-bipyridine,[17] and 6,6′-dimethoxyl-2,2′-bipyridine[18] were synthesized according to the previously reported procedures.

Catalytic conversion of LA into GVL with hydrogen: LA (5 mmol), aqueous solution of catalyst (0.5 mmol L^{-1}, 1 mL), and water (4 mL) were added to a 10 mL zirconium alloy high-pressure reaction tube, and stirred at a rate of 800 rpm under 1.01 MPa H_2 for the specified reaction time. The mixture of substrates and catalyst were heated to the desired temperature in less than 15 min. The liquid products were diluted with methanol and analyzed by using GC on a Shimadzu GC-2014 gas chromatograph equipped with a capillary column (DM Waxm 30 m × 0.25 mm) and a flame ionization detector. The identification of the products was performed by using GC–MS. An internal standard (dimethyl formamide) was used to determine the amount of GVL produced.

Catalytic conversion of LA into GVL with FA: LA (5 mmol), FA (6–10 mmol), aqueous solution of catalyst (0.5 or 5 mmol L^{-1}, 1 mL), and water (4 mL) were added to a disposable tube with a plastic screw cap top. The catalytic conversion proceeded as described above, but in the absence of hydrogen.

Dehydration of carbohydrate biomass with H_2SO_4 and subsequent hydrogenation: Carbohydrate, that is, cellulose, starch, sucrose, glucose, or fructose (0.9 g) was loaded into a 25 mL Hastelloy-C high-pressure Parr reactor, and H_2SO_4 (5 mL, 0.5 mol L^{-1}) was then added. Under 0.507 MPa N_2, the autoclave was quickly heated to 170 °C, and vigorously stirred for 1 h. After the reaction, the insoluble solid byproducts were removed through filtration. The hydrolysis filtrate containing LA and FA (4 mL) was transferred to a 10 mL zirconium alloy high-pressure reaction tube containing an aqueous solution of catalyst **6** (1 mL, 0.5 mmol L^{-1}), which was then heated to 120 °C with 1.01 MPa H_2 for 4 h. Finally, the products were analyzed by using GC as described above. The concentrations of LA and FA were determined by using HPLC; this system consisted of a Waters 1525 pump, a Waters 5C18-PAQ column (4.6×250 mm), and a Waters 2414 refractive index detector. H_2SO_4 (5 mM) was used as the mobile phase at flow rate of 1 mL min^{-1}.

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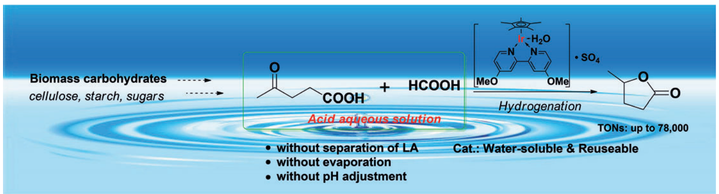
Conversion of Carbohydrate Biomass to γ-Valerolactone by using Water-Soluble and Reusable Iridium Complexes in Acidic Aqueous Media



Mild-mannered manipulation: A catalytic method for the conversion of carbohydrate biomass to γ-valerolactone in acidic aqueous media has been developed. The water-soluble iridium complexes were observed to be extremely catalytically active for providing γ-valerolactone in high yields with high *TON*s. The homogeneous catalysts can also be recycled and reused by applying a simple phase separation process.