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Highly Efficient Hydrogenation of Levulinic Acid into γ-Valerolactone with an Iron Pincer Complex

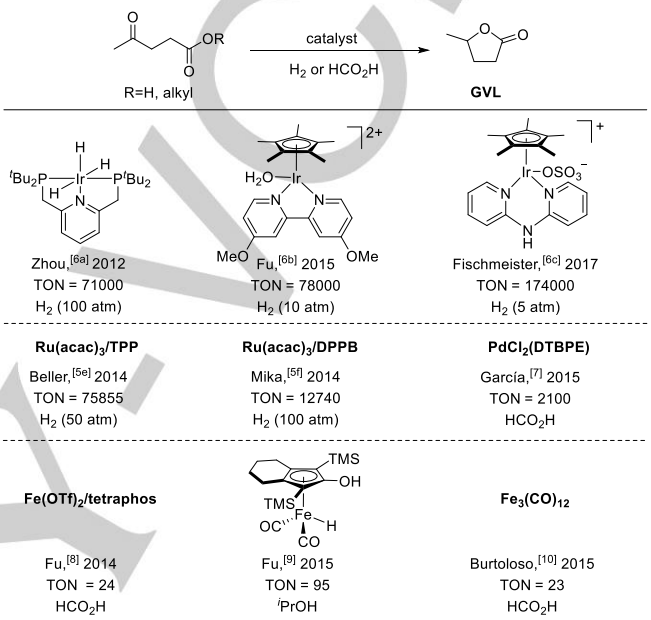
Yuxuan Yi,[a] Huiying Liu,[a] Ling-Ping Xiao,[a] Bo Wang[a] and Guoyong Song*[a]

Abstract: The search for nonprecious metal catalysts for the synthesis of γ-valerolactone (GVL) through hydrogenation of levulinic acid and its derivatives in an efficient fashion is of great interest and importance, as GVL is an important a sustainable liquid. We herein report a pincer iron complex can efficiently catalyze the hydrogenation of levulinic acid and methyl levulinate into GVL, achieved up to 23000 turnover numbers and 1917 h^{-1} turnover frequencies. This iron catalyst also enabled the formation of GVL from various biomass-derived carbohydrates in aqueous solution, thus paving a new way toward a renewable chemical industry.

Introduction

The depletion of fossil fuels with increasing emission of carbon dioxide has led to the search for alternative sustainable energy and chemicals sources such as biomass.[1] As a sustainable liquid, γ-valerolactone (GVL) has attractive physical and chemical property and is used as solvent, flavoring agent and a precursor for high-value chemicals and fuels.[2] In the presence of a heterogeneous or homogeneous metal catalyst, levulinic acid (LA), which is produced by acid-catalyzed hydrolysis of cellulose to glucose followed by *in situ* isomerization (to form fructose), dehydration (to form 5-HMF) and deformylation in a biorefinery process,[1] can be converted into GVL through hydrogenation and dehydrative ring closure.[3] As a consequence, the development of efficient, economical catalytic processes for preparation of GVL from levulinic acid has received intensive attention.[3-7]

Compared to heterogeneous catalysts,[3,4] homogeneous catalysts have high catalytic efficiency towards hydrogenation of levulinic acid or levulinate esters and turnover numbers (TON) of approximately 174000 has been achieved (Scheme 1).[3,5-7] The most efficient catalysts are typically based on precious and heavy metals such as ruthenium[5], iridium[6] and palladium[7]. In comparison, the same transformation with nonprecious, earth-abundant metal catalysts is a relatively unexplored area in literature.[8-10] Fu and co-workers showed that Casey's catalyst and the combination of $Fe(OTf)_2$ with a tertraphosphine ligand could catalyze the conversion of levulinate esters into GVL.[8,9] Burtoloso and co-workers reported $Fe_3(CO)_{12}$-catalyzed hydrogenation of LA, thus giving GVL in a high yield with TON of 23.[10] Noticeably, compared to reported Ru or Ir-based catalysts, the catalytic activities of nonprecious metal catalysts are too low to use in a practical manner, whereas the TON do not exceed 100 (Scheme 1). Therefore, the search of non-precious metal catalysts enables the advancement this transformation in a high efficient fashion is of great interest and importance.



Scheme 1. Transition metal catalysts for hydrogenation of LA to GVL. (TPP = (1,2-(bis-di-tert-butylphospino)ethane), DPPB = 1,4-bis (diphenylphosphino) butane, DTBPE = 1,2-bis(ditertbutylphosphino)ethane, tetraphos = tris((2-diphenylphosphino)ethyl)phosphine)

Several group recently described that the iron complexes supported on a PNP-pincer ligand (such as **1**-**4** in chart 1 and related species) can act as efficient catalysts for de/hydrogenation transformations.[11-15] In 2011, Milstein reported that a pincer iron complex **1** was capable of 1880 turnover numbers in hydrogenation of ketones.[12a] In 2013, Beller and co-workers used an aliphatic PNP-Fe complex **2** for reforming of methanol to produce H_2 and CO_2 with TON of nearly 10000.[13a] Fairweather and Guan found that the borohydride analog of **2** could catalyze hydrogenation of esters to form alcohols.[13b] Milstein[12b], Hazari and Bernskoetter[13h], Kirchner and Gonsalvi[14b] independently demonstrated that iron complexes embedded in a PNP-pincer ligand efficiently catalyzed the hydrogenation of CO_2 to formate, achieved up to 60000 turnover numbers.[13h]

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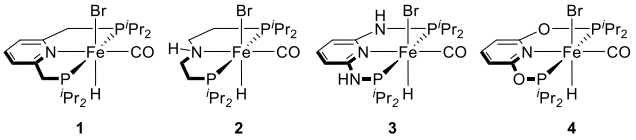


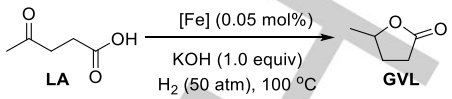
Chart 1. Selected examples of PNP-pincer iron complexes

We envisioned that the pincer Fe complexes might serve as unique catalysts for preparation of GVL through hydrogenation of LA. Herein, we report that hydrogenation of levulinic acid and methyl levulinate (ML) catalyzed by iron complexes with pincer ligands, thus yielding GVL in excellent yield (up to 97%) with turnover numbers up to 23000 and turnover frequencies up to 1917 h^{-1} under relatively mild reaction conditions. This iron catalyst is also compatible with the levulinic acid aqueous solution generated from carbohydrates hydrolysis, to afford GVL in high yields.

Results and Discussion

At first, we examined the hydrogenation reaction of levulinic acid by using a series of iron pincer complexes (Chart 1) in MeOH at 100 °C, 50 atm H_2 in the presence of 1.0 equiv of KOH.[16] Significant influence of the ligands was observed (Table 1), suggesting that an appropriate pincer ligand is highly important for this reaction. The Fe complex **1** (0.05 mol %) bearing a bis(diisopropyl-phosphinomethyl)pyridine ligand[12] afforded GVL in 90% yield in 2 h (Table 1, entry 1), while the aliphatic PNP-Fe **2**[13] gave a low yield of 27% (entry 2). When complex **3**,[14] which ligates a 2,6-diaminopyridine scaffold, was used as a catalyst, the yield of GVL improved to 97% with a turnover numbers of 1940 and a turnover frequencies of 970 h^{-1} (entry 3). In contrast, complex **4** embedded in 2,6-bis(phosphinito)pyridine backbone,[15] does not show any activity (entry 4).[17] This could be because the acidic CH_2 or NH spacer in **1-3** pincer ligands can assist the formation of a five-coordinated Fe hydride specie through an acid-base reaction,[12-14] while the O linker in complex **4** prevents such a possibility.[18,19] The combination of **3** and AgOTf, which possibly leads to the cationic iron specie,[12b] is capable of the formation of GVL in high yield in the presence of 1.0 equiv KOH. On the contrary, no GVL was observed when catalytic KOH (0.1 equiv) was used (entries 5-6), suggesting that the cationic iron specie may be not involved in current catalytic cycle.[19] A control experiment without catalyst led to only methyl levulinate in *ca*. 40% yield, suggesting that ML is a possible intermediate in methanol.[3c] On the basis of the catalyst screening results, solvents screening was then studied with complex **3**. Analogous to the case for MeOH, the hydrogenation reaction in EtOH, ^{i}PrOH, THF/H_2O (1/4) and water proceeded to give GVL in 90-94% yields (entries 7-10). When neat THF was used, the yield was decreased to 15% in 12 h, indicating the need for a protic solvent (entry 11). Of note, 4-hydroxypentanoic acid could be detected as an possible intermediate in protic solvent (see SI), which can be converted into GVL through ring closure under catalyst-free condition.[4e,18]

Table 1 PNP-Fe-catalyzed hydrogenation of levulinic acid into *γ*-valerolactone[a]



Entry	[Fe]	Solvent	Time (h)	Yield[b] (%)	TON	TOF (h^{-1})
1	**1**	MeOH	2	90	1800	900
2	**2**	MeOH	5	27	540	270
3	**3**	MeOH	2	97(95[c])	1940	970
4	**4**	MeOH	12	0		
5[d]	**3**/AgOTf	MeOH	2	95	1900	950
6[e]	**3**/AgOTf	MeOH	12	0		
7	**3**	EtOH	5	92	1840	368
8	**3**	^{i}PrOH	2	94	1880	940
9	**3**	THF/H_2O	2	90	1800	900
10	**3**	H_2O	2	90	1800	900
11	**3**	THF	12	15	300	25

[a] Reaction conditions: levulinic acid (580 mg, 5 mmol), [Fe] (0.05 mol %), KOH (280 mg, 5 mmol), solvent (2 mL), H_2 (50 atm). [b] GC yield using *N*-methyl pyrrolidone (NMP) as an internal standard. [c] An anhydrous KOH reagent where the KOH composition was determined as 91% was used. [d] 0.1 mol % AgOTf was added. [e] 0.1 equiv KOH was used.

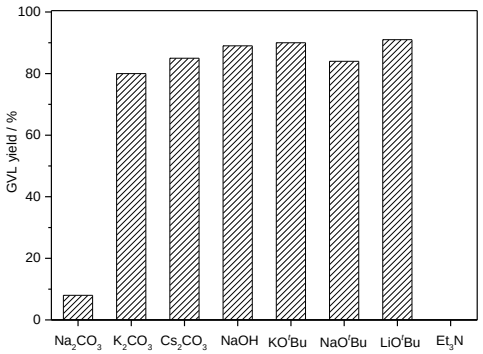


Figure 1. The effect of base for **3**-catalyzed hydrogenation of LA (reaction conditions: levulinic acid (580 mg, 5 mmol), **3** (0.05 mol %), base (5 mmol), MeOH (2 mL), H_2 (50 atm), 5 h.

A screening of the effect of base for **3**-catalyzed hydrogenation of LA was carried out (Figure 1, see also SI). Performing the reaction by using NaOH, K_2CO_3 and Cs_2CO_3 gave GVL in desirable yields. Changing the base from KOH to Na_2CO_3 led to a lower yield of GVL (8%) under analogous

reaction conditions. In the case of 1.0 equiv of KO^{t}Bu, NaO^{t}Bu or LiO^{t}Bu, 0.05 mol% of complex **3** was capable of hydrogenating LA to GVL with 84-91% yields. GVL was not formed using either TEA (triethylamine) or DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), probably because the weak base does not enable the formation of a five-coordinated Fe−H through an acid-base reaction.[14a] It is worth noting that when sub-stoichiometric KOH (such as 0.9 equiv) was used,[16] only methyl levulinate was obtained (*ca*. 42% yield), with no observation of hydrogenation product, attributing to the fact that excess LA inhibits the formation of five-coordinated Fe species.[14a] We tested the reactions in water with different amounts of base. In the case of 0.9 equiv KOH (where pH is *ca*. 6.0), no GVL was generated, being contrasts with the observation of 1.0 equiv KOH dosage (where pH is *ca*. 14 and GVL yield is 90%). These results confirmed again that the five-coordinated iron active specie could only be generated under basic condition.

The hydrogenation reaction of LA was further carried out over **3** in MeOH under 50 atm H_2 at different temperatures, as shown in Figure 2. To our surprise, the reaction proceeded even at room temperature with 0.05 mol% Fe catalyst, giving GVL in 71% yield in 5 h and 95% yield in 15 h, respectively. Increasing the temperature to 150 °C, a drop in activity was observed (61%) probably because of the decomposition of iron complex. The influence of H_2 pressure of 0.05 mol% complex **3** at 100 °C was also investigated (Figure 2). No transfer hydrogenation reaction of LA was observed in the absence of H_2 and only 5% GVL was observed after 48 h under 1 atm H_2. In 5 h reaction time situation, the reduction of LA seemed to slightly depend on the hydrogen pressure above 40 atm, and became independent over 50 atm, which is consistent with previous report for reduction of LA by using the combination of $Ru(acac)_3$ and sulfonated-phosphine ligand.[5d] In the case of a relative low H_2 pressure (10 atm), **3**-catalyzed hydrogenation of LA as a function of time at 100 °C was performed, from which 38%, 50% and 96% yield of GVL were obtained in 2 h, 5 h and 15 h, respectively. These results indicated that the catalyst can keep

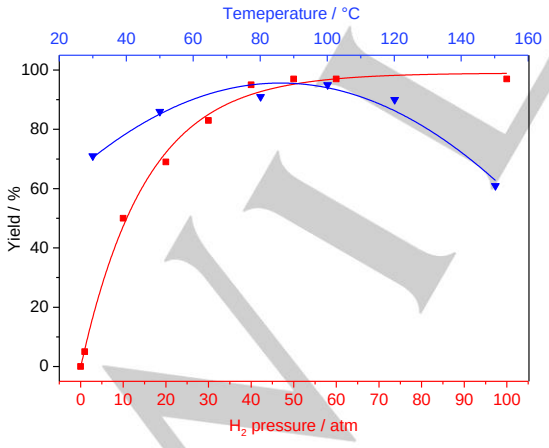


Figure 2. The influences of temperature (blue line) and H_2 pressure (red line) for **3**-catalyzed hydrogenation of LA during 5 h. (Reaction conditions: levulinic acid (580 mg, 5 mmol), **3** (0.05 mol %), KOH (5 mmol), MeOH (2 mL); for temperature line, H_2 pressure is 50 atm; for H_2 pressure line, reaction temperature is 100 °C).

alive during 15 h under such conditions and the solubility of H_2 may dominate the rate of hydrogenation of LA.

The attempt to reuse the catalyst through either isolation of iron complex or addition of more LA to the reaction mixture is not successful, probably because the active iron specie is readily decomposed. We then focused on the evaluation of the potential of complex **3** in reduction of LA by using low catalyst dosage in MeOH. In the presence of 0.01 mol% of **3**, GVL was formed in 40% yield at 50 atm H_2; increasing the H_2 pressure to 100 atm led to an excellent GVL yield (91%) with a 9100 TON after 12 h (Table 2, entries 1 and 2). On further reduction of the catalyst loading to 0.002 mol%, hydrogenation of LA (50 mmol, 5.8 g) was still achieved with a high TON of 23000 and TOF of 1917 h^{-1}, albeit in moderate yield (46%) (entry 4). Lowering the catalyst dosage further (0.001 mol %) under the same conditions led to a lower yield (10%) and TON of 10000 (entry 7). The catalytic activity of complex **3** with 0.002 mol % dosage was also tested in H_2O and ^{i}PrOH, which gave GVL in 45% and 23% yields, respectively (entries 6 and 7). The observed activity of **3** is comparable to some reported precious metal catalysts, such as PNP-pincer iridium complex (TON: 71000, TOF: 1480 h^{-1}),[6a] Ru/DPPB (TON: 12740, TOF: 7077 h^{-1}),[5f] and [Pd(DTBPE)Cl_2] (TON: 2100, TOF: 2100 h^{-1}).[7]

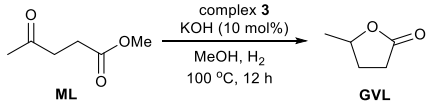
Table 2. Hydrogenation of LA to GVL with **3** on larger scale.[a]

Entry	LA (mmol)	**3** (mol %)	H_2 (atm)	Yield (%)	TON	TOF (h^{-1})
1	10	0.01	50	40	4000	333
2	10	0.01	100	91	9100	758
3	20	0.005	100	70	14000	1166
4	50	0.002	100	46	23000	1917
5	50	0.001	100	10	10000	833
6[b]	50	0.002	100	45	22500	1875
7[c]	50	0.002	100	23	11500	958

[a] Reaction conditions: [LA] = 2.5 mol/L in MeOH, 1.0 equiv of KOH, 100 °C, 12 h. [b] [LA] = 2.5 mol/L in H_2O. [c] [LA] = 2.5 mol/L in ^{i}PrOH.

When methyl levulinate (ML) is utilized instead of LA under the similar reaction conditions, GVL could be formed by using catalytic amount of KOH. At 50 atm H_2 and 100 °C, hydrogenation of ML with 0.05 mol% of **3** and 0.1 equiv of KOH afforded GVL in 70% and 85% yield after 5 h and 12 h respectively (Table 3, entries 1 and 2). In the case of low dosage of **3** (0.002 mol%), a drop in GVL yield (11%) was observed, while increasing KOH to 1.0 equiv resulted in GVL in 44% yield with TON as 22000 and TOF as 1833 h^{-1}. Obviously, the production of GVL from ML with complex **3** under hydrogen is more efficient than previously reported iron catalysts under transfer hydrogenation conditions[9] or using formic acid as hydrogen source.[8,10]

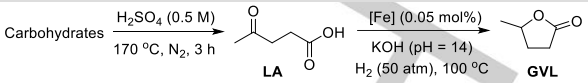
Table 3. Hydrogenation of methyl levulinate into *γ*-valerolactone with **3**.[a]



Entry	ML (mmol)	**3** (mol%)	H_2 (atm)	Time (h)	Yield (%)	TON	TOF (h^{-1})
1	5	0.05	50	12	85	1700	141
2	5	0.05	50	5	70	1400	280
3	10	0.01	100	12	81	8100	675
4	25	0.005	100	12	45	9000	750
5[b]	25	0.005	100	12	67	13400	1116
6	50	0.002	100	12	11	5500	458
7[b]	50	0.005	100	12	44	22000	1833

[a] Reaction conditions: [ML] = 2.5 mol/L in MeOH, 100 °C. [b] 1.0 equiv of KOH was used.

Table 4. Dehydration of carbohydrates[a] and subsequent reduction of carbohydrate-derived LA with 3.[b]



Entry	Carbohydrate	LA yield (%)[c]	GVL yield(%)[d]
1	fructose	50	48 (96)
2	glucose	47	45 (96)
3	sucrose	45	43 (95)
4	starch	31	29 (94)
5	cellulose	24	23 (96)

[a] Reaction conditions: carbohydrate (1.8 g), H_2SO_4 aqueous (0.5 M, 10 mL), N_2, 170 °C, 3 h. [b] Reaction conditions: filtrate from hydrolysis with pH value as 14, complex **3** (0.05 mol%), 100 °C, 5 h. [c] Yields based on carbohydrate. [d] Overall yield for the two-stage conversion of carbohydrate. The yield of LA is given in parenthesis.

Since levulinic acid is available from carbohydrates via hydrolysis, dehydration and deformylation,[1] we then explored the direct conversion of upstream substrates into γ-valerolactone by using iron complex **3** (Table 4). The treatment of fructose with H_2SO_4 in water at 170 °C led to an acidic aqueous solution containing LA (50% yield).[6b,21] After filtration and alkalization with KOH, the LA could converted into GVL in the presence of complex **3** (0.05 mol%) at 100 °C and 50 atm H_2 in 5 h quantitatively (Table 4, entry 1). Glucose and sucrose were compatible with the combined procedure, to afford GVL with overall yields of 45% and 43%, respectively (entries 2-3). In the case of polymeric carbohydrates, a drop in formation of levulinic acid was observed, as seen in the case of starch (31%) and cellulose (24%), while the activity of **3**-catalyzed hydrogenation of LA remained high (94% and 96%) (entries 4-5). These results indicated that complex **3** could be used for the generation of GVL from carbohydrate biomass resources with the addition of hydrogen, without the need for separation of LA.

Conclusions

In summary, we report that iron complexes having a pincer PNP ligand can serve as an excellent catalyst for hydrogenation of levulinic acid and methyl levulinate into *γ*-valerolactone, where turnover numbers of approximately 23000 and turnover frequencies of 1917 h^{-1} were achieved. The catalyst also showed high activity for formation of GVL from LA aqueous solution generated from various biomass-derived carbohydrates. This high performance of these iron-based non-precious catalysts highlights the enormous potential for possible applications in biomass conversion.

Experimental Section

All the reaction dealing with air or moisture-sensitive compounds were performed by standard Schlenk techniques or in the nitrogen-filled glovebox. The iron complexes **1**-**4** were prepared according to reported literatures,[12-16] and were used as catalyst in the crystal form after recrystallization. GC-MS analysis (Shimadu GCMS-QP2010SE) equipped with a HP-5 MS (30 m × 0.25 mm × 0.25 μm) column. GC analysis were obtained on a Shimadzu Model 2010 plus equipped with a HP-5 column (30 m × 0.25 mm × 0.25 μm) using a flame ionization detector (FID). HPLC analysis was conducted on an Agilent 1260 chromatography system equipped an Aminex HPX-87H column.

General procedure for hydrogenation of LA to GVL: In a glove-box, levulinic acid (581 mg, 5 mmol), KOH (330.1 mg, 85 % purity, 5 mmol), complex **3** (1.3 mg, 2.5 μmol) and MeOH (2 mL) were charged into a steel autoclave. The autoclave was tightened and flushed with hydrogen three times and finally charged with hydrogen at 50 atm. The reaction mixture was stirred (600 rpm) at 100 °C for desired time. After reaction, the autoclave was cooled to room temperature and the pressure was released carefully. After acidification, *N*-methyl-pyrrolidinone (NMP) was added as a standard. The identification and quantification of the products was performed on GC-MS and GC.

Dehydration of carbohydrates with H_2SO_4 and subsequent hydrogenation: Carbohydrate (1.8 g) and 0.5 M H_2SO_4 (10 mL) were loaded in a Teflon-lined stainless steel autoclave, which was heated at 170 °C under N_2 atmosphere for 3 h. After removal the insoluble fraction by filtration, KOH was added to the solution until pH value reached to 14. The aqueous solution was then transferred to the 50 mL autoclave reactor containing complex **3** (0.05 mol%, based on the yield of LA from carbohydrate, which was determined by HPLC), which was then charged with hydrogen at 50 atm and heated to 100 °C for 5 h. The GVL was analyzed by using GC as described above.

Acknowledgements

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Keywords: levulinic acid • *γ*-valerolactone • iron • pincer • hydrogenation

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[19] In current reaction system, the reaction of LA with a base is prior to the formation of the five-coordinated Fe hydride (the catalytical active specie) through the acid-base reaction of NH spacer in ligand and coordinated bromide with a base.

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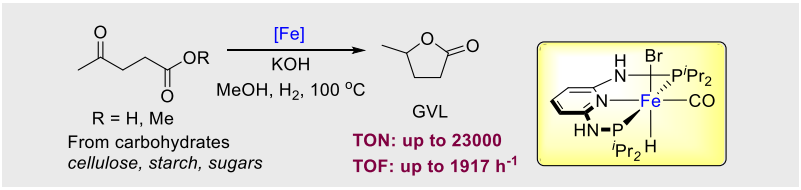

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Page No. – Page No.

Highly Efficient Hydrogenation of Levulinic Acid into γ-Valerolactone with an Iron Pincer Complex

A pincer iron complex can serve as an excellent catalyst for preparation of *γ*-valerolactone *via* hydrogenation of levulinic acid and methyl levulinate, achieving up to 23000 turnover numbers and 1917 h^{-1} turnover frequencies.