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ARTICLE TYPE

Improved catalyst system for the reduction of levulinic acid to γ -valerolactone

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An improved bidentate phosphine modified recyclable catalyst system was developed for the selective conversion of biomass-derived levulinic acid into γ -valerolactone with TOF of 21233 h⁻¹ in a solvent-, chlorine- and additive-free reaction environment.

Currently, fossil resources provide more than 95% of our energy needs and feedstock of chemical industry. Their replacement is one of the most challenging tasks of this generation. Especially, the production of carbon-based chemicals from sustainable resources has become a key issue for the chemical industry. The intensive research activities on biomass conversion has led to the identification of unique platform molecules such as 5-hydroxymethyl furfural (5-HMF),¹ and γ -valerolactone (GVL).² These small molecules can replace the currently used fossil-based chemicals or serve as renewable feedstock for their production. Due to its outstanding physical and chemical properties, GVL was suggested to be a sustainable liquid by Horváth *et al* in 2008.^{2,3} Subsequently, GVL was used for the production of transportation fuels,⁴ butane isomers,^{4b} octane booster,² alkanes,⁵ 2-methyl-tetrahydrofuran,⁵ pentane-1,4-diol,^{5,15a} ionic liquids,⁶ adipic acid,⁷ alkyl valerates,^{6a} polymers,⁸ pentanoic acid,⁹ or as a solvent.¹⁰

Obviously, the most effective protocol to manufacture GVL is the selective hydrogenation of levulinic acid (LA).¹¹ LA is another platform molecule which can be obtained via 5-HMF by acid-catalysed dehydration of hexoses, a major component of biomass (Fig. 1). Noteworthy, it was shown that GVL can be used as a green solvent for the hydrolysis of fructose, the precursor of 5-HMF.¹² Although, heterogeneous catalysts can be easily removed from the reaction mixtures, their activities are relatively low. Thus, high temperature and pressure, moreover a co-catalyst and/or a proper solvent is necessary to obtain satisfactory conversion.¹³ On the other hand, homogeneous catalysts exhibit higher activity and selectivity. Consequently, the development of a simple, highly efficient catalyst for the reduction of LA to GVL has an utmost importance.¹⁴ Leitner and co-workers reported the application of Ru/TriPhos catalysts for the efficient and selective production of GVL, 1,4-pentanediol and methyltetrahydrofuran in the presence of different additives such as NH₄PF₆.¹⁵ The pincer ligand-modified iridium complexes were also found to be active catalyst (TOF = 1480 h⁻¹) for hydrogenation of LA in the presence of base (*e.g.* NaOH or KOH) in alcohols (*e.g.* EtOH, iPrOH).¹⁶

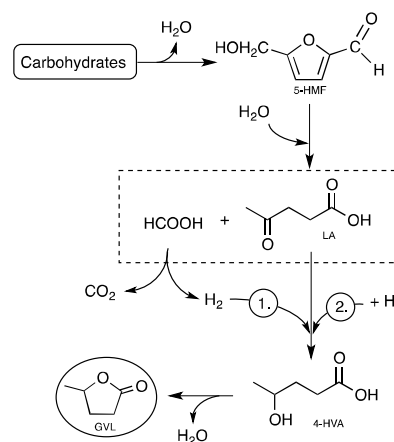


Fig. 1 Carbohydrates conversion

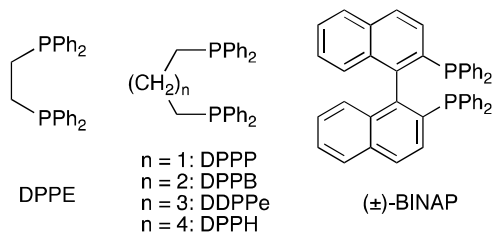
Recently, similarly active (TOF = 2160 h⁻¹) iridium complexes with 2,2'-bipyridine derivatives were reported for the reduction of LA under mild reaction conditions in water using [LA] = 1 mol dm⁻³ initial concentration,¹⁷ *n.b.* in spite of the high activity, the final product concentration is less than 1M and the water-removal step results in low energy efficiency of the process. We have demonstrated, that LA can be selectively and quantitatively reduced to GVL in the presence of a catalyst *in situ* generated from Ru(acac)₃ and 10 eq of tertiary sulfonated phosphines without using any solvent or additive with TOF = 1440–3538 sec⁻¹.¹⁸ It should be noted that this system was also found to be active under continuous conditions as well.¹⁹

During the decomposition of carbohydrates, LA and formic acid are formed in equimolar amount. Thus, formic acid can be used as hydrogen source for the reduction LA and spontaneous lacton formation to GVL. Horváth and co-workers reported that LA was converted to GVL by using a complex catalyst [(η^6 -C₆Me₆)Ru(bpy)(H₂O)][SO₄] at 70 °C.⁵ Recently, GVL was quantitatively prepared *via* transfer hydrogenation by using HCOOH in the presence of Shvo-type catalysts such as {[2,5-Ph₂-3,4-Ar₂-(η^5 -C₅O)₂H]Ru₂(CO)₄(μ -H)} [Ar = p-MeOPh, p-MePh, and Ph] at 100 °C without any additive.^{20,21} Deng *et al* reported a RuCl₃/PPh₃ catalyst system for transfer hydrogenation of LA to GVL, however this required the addition of base *e.g.* pyridine, LiOH, NEt₃ resulting in GVL with yield of 16 – 95%.²²

Here it is proposed, that the activity of the Ru-based catalyst

systems can be increased by the application of bidentate phosphine ligands retaining the environmentally benign benefits of a solvent-free system.

Firstly, LA was attempted to be reduced by Ru(III)-acetylacetonate in the absence of phosphine ligands. Expectedly, no conversion was detected after 2 h (Table 1, entry 1). Sulfonation of $n\text{BuP}(\text{C}_6\text{H}_5)_2$, a malodorous, colorless liquid, results in the formation of solid $n\text{BuP}(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})_2$ (Bu-DPPDS) ligand with similar electronic and steric properties compared to $n\text{BuP}(\text{C}_6\text{H}_5)_2$. For the selective conversion of LA to GVL, the highest activity of the Ru catalyst modified with monodentate phosphine ligand, was achieved by applying Bu-DPPDS under 100 bar H_2 at 140 °C (Table 1, entry 2).¹⁸ It was



Scheme 1 Bidentate phosphine ligands

revealed that the hydrogenation activity of the Ru catalysts can be significantly enhanced by the use of chelating type bidentate $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1 - 3$) ligands.²³

Thus, we compare the activity of Bu-DPPDS analogue, $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ (Scheme 1, DPPB) modified Ru catalyst for the reduction of LA. Quantitative conversion of LA to GVL for 1 h ($\text{TOF} = 6370 \text{ h}^{-1}$) under identical conditions was obtained (Table 1, entry 3). It has been shown, that the catalytic activity was strongly influenced by the phosphine content of the reaction mixture. Furthermore, the activity was also influenced by the number of the methylene spacers between the phosphorus atoms of the bidentate ligands *e.g.* by the size of the chelate ring of the active form of the catalyst. Consequently, the hydrogenation was repeated at lower catalyst concentration in the presence of various bidentate ligands (Table 1, entries 4–8). It was shown, that activity was negligible when DPPE was applied, whereas it was similar to the Bu-DPPDS modified system by the use of DPPP. In the case of DPPB, quantitative formation of GVL was detected within 1 h (Table 1, entry 6) representing an outstanding activity ($\text{TOF} = 7077 \text{ h}^{-1}$). By increasing the number of methylene spacer in the ligand, *i.e.* the size of the chelate ring on the catalytically active species generated *in situ* from $\text{Ru}(\text{acac})_3$ and ligands, the activity started to decrease. The DDDPe showed similar activity than that of Bu-DPPDS and it was below 2000 h^{-1} in the case of DPPH. Due to the six CH_2 units, DPPH could act as a monodentate phosphine. To achieve further improvement in TOF by optimizing the ligand concentration in the reaction mixture, we investigated the reduction of LA by using Ru/DPPB catalyst in the concentration range of $[\text{DPPB}] = 0.77 \times 10^{-3} - 15.4 \times 10^{-3}$ at constant Ru content of $0.775 \times 10^{-3} \text{ mol dm}^{-3}$ ($8 \times 10^{-3} \text{ mol}\%$). Expectedly, the ligand content had strong influence on the formation of GVL as shown in Fig. 2. When equimolar amount or 2.5-fold excess of ligand was used, conversions of 4.5 and 12 % were detected. Significant increase in the rate was observed at ratios of DPPB/Ru between 5–10 followed by slight decrease at

higher ratios. The concentration dependence curve shows a maximum at $[\text{DPPB}] = 7.75 \pm 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, which corresponds to the ligand/Ru = 10 ± 1.0 . This is in good agreement with our previous report for Bu-DPPDS¹⁸ and for the ligand-excess favored reduction of carbonyl groups.²⁴ The ligand exchange equilibrium between the catalyst species and free ligand — depending on pressure, temperature *etc.* — determines the optimal ligand concentration in the reaction mixture. Furthermore, due to the presence of a bidentate ligand, the reversible arm-off dissociation cannot be excluded either.²⁵ The GC and NMR measurements of the conversion of 293.02 mmol of LA in the presence of catalyst *in situ* formed from $\text{Ru}(\text{acac})_3$ (0.023 mmol) and of DPPB (0.23 mmol) proved that no by-product formation, including over-hydrogenated products

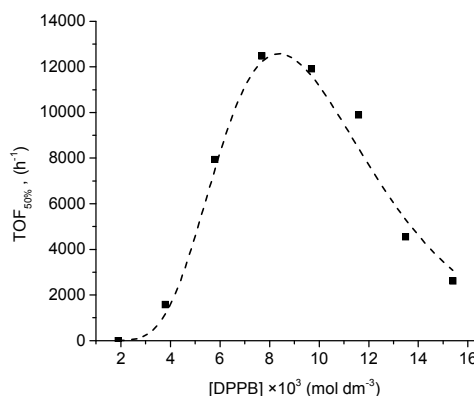


Fig. 2 Turnover frequencies ($\text{TOF}_{50\%}$ = mole of LA per mol of Ru per hour at 50% conversion) at different DPPB concentrations. Reaction conditions: $[\text{Ru}] = 0.775 \times 10^{-3} \text{ mol dm}^{-3}$ ($8 \times 10^{-3} \text{ mol}\%$), 100 bar H_2 , 140 °C.

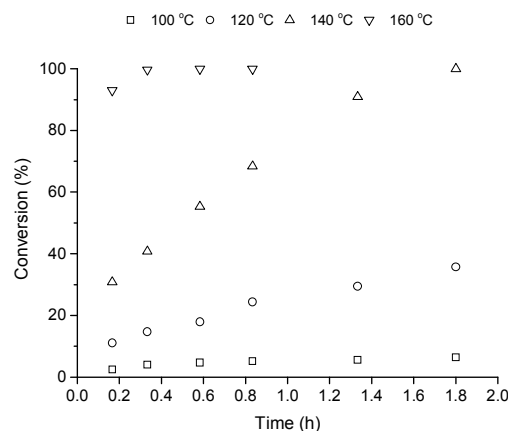


Fig. 3 Conversion of LA to GVL at different temperatures. Conditions: $[\text{Ru}] = 0.775 \times 10^{-3} \text{ mol dm}^{-3}$ ($8 \times 10^{-3} \text{ mol}\%$), $[\text{DPPB}] = 7.75 \times 10^{-3} \text{ mol dm}^{-3}$, 100 bar H_2 .

such as 2-methyltetrahydrofuran, could be detected. The ^{31}P -NMR spectrum of final reaction mixture did not indicate the formation of phosphine oxide and any sign of decomposition of the ligand. Since these types of ligands are solid, thus nosulfonation was necessary. Finally, the binaphthyl derivative (±)-BINAP, which could also form a seven-member chelate ring with Ru center, similarly to the DPPB, was also investigated. However, the activity were similar to those obtained by the use

Table 1 Hydrogenation of levulinic acid in the presence of phosphine ligands.

| Entry | [Ru] × 10 ³ (mol dm ⁻³) | Ligand | [Ligand] × 10 ³ (mol dm ⁻³) | T (°C) | P(H ₂) (bar) | Time (h) | Yield (%) | TON | TOF (h ⁻¹) |
|----------------|---|-----------|---|-----------|-----------------------------|-------------|--------------|-------|---------------------------|
| 1 | 1.55 | - | - | 140 | 100 | 2.0 | 0 | 0 | 0 |
| 2 ^a | 1.55 | Bu-DPPDS | 15.5 | 140 | 100 | 1.8 | >99.9 | 6370 | 3538 |
| 3 ^a | 1.55 | DPPB | 15.5 | 140 | 100 | 1.0 | >99.9 | 6370 | 6370 |
| 4 | 0.775 | DPPE | 7.75 | 140 | 100 | 1.8 | 1.8 | 226 | 125 |
| 5 | 0.775 | DPPPr | 7.75 | 140 | 100 | 1.8 | 57.5 | 7325 | 4069 |
| 6 | 0.775 | DPPB | 7.75 | 140 | 100 | 1.8 | >99.9 | 12740 | 7077 |
| 7 | 0.775 | DPPPe | 7.75 | 140 | 100 | 1.8 | 51.2 | 6522 | 3623 |
| 8 | 0.775 | DPPH | 7.75 | 140 | 100 | 1.8 | 25.3 | 3223 | 1790 |
| 9 | 0.775 | (±)-BINAP | 7.75 | 140 | 100 | 1.8 | 98.6 | 12561 | 6978 |
| 10 | 0.775 | DPPB | 7.75 | 140 | 75 | 1.8 | >99.9 | 12740 | 7077 |
| 11 | 0.775 | DPPB | 7.75 | 140 | 50 | 1.8 | >99.9 | 12740 | 7077 |
| 12 | 0.775 | DPPB | 7.75 | 140 | 25 | 1.8 | >50.6 | 6446 | 3581 |
| 13 | 0.775 | DPPB | 7.75 | 140 | 10 | 1.8 | 26.3 | 3350 | 1861 |
| 14 | 0.775 | DPPB | 7.75 | 140 | 10 | 4.5 | 70 | 8918 | 1981 |
| 15 | 0.775 | DPPB | 7.75 | 160 | 100 | 0.6 | >99.9 | 12740 | 21233 |
| 16 | 0.775 | DPPB | 7.75 | 120 | 100 | 1.8 | 35.7 | 4548 | 2526 |
| 17 | 0.775 | DPPB | 7.75 | 100 | 100 | 1.8 | 6.4 | 815 | 453 |

^a Conditions from Ref. 18. Reaction conditions: 30 mL (293.02 mmol) LA, Ru precursor: Ru(acac)₃, Ligand/Ru = 10, TON defined as mol of substrates converted per mol of Ru.

5 the less expensive DPPB (Table 1, entry 6).

The effect of the hydrogen pressure on the GVL formation was also determined in the range of 10–100 bar using Ru/DPPB system (Table 1, entries 6, 10–14). As was shown for the Ru/DPPDS system,¹⁸ the conversion rate was not affected by 10 reducing the pressure to 50 bar for 1.8 h, however, further decreasing the pressures (25 and 10 bar) the reaction rates decreased significantly.

The investigation of the effect of reaction temperature (Fig. 3., Table 1, entries 6, 15–17) showed, that the conversions were 15 negligible at 100 °C and modest at 120 °C. By increasing the temperature to 160 °C, full conversion was obtained for 0.6 h, corresponding to TOF = 21233 h⁻¹. To our best knowledge, so far it is the highest TOF value obtained for a selective homogeneous hydrogenation of LA to GVL.

20 The recyclability of the Ru(acac)₃/DPPB catalyst was investigated under batch conditions using [Ru] = 1.55 × 10⁻³ mol dm⁻³ (0.16 mol%) and [DPPB] = 0.15 mol dm⁻³ under 100 bar of H₂ at 140 °C.¹⁸ Full conversion of LA to GVL was detected in the first run resulting in light orange solution after 30 min (ESI Pict 25 S1†). The volatile compounds were removed by vacuum transfer (4–6 Hgmm) by the use of a 20-cm column resulting in a clear solution. The orange glue-like residue (ESI Pict S2†) was completely dissolved in 30 mL (293.02 mmol) of LA. Noteworthy, no phosphorous compounds were detected in the 30 distillate. The ¹H-NMR and GC analysis proved that the distillate was pure GVL. The light orange solution (ESI Pict S3†) was transferred into the reactor followed by pressurizing to 100 bar H₂. The reaction was started by increasing the temperature up to 140 °C. A significant pressure drop indicated the reduction 35 process. After a similar workup of the initial run, the second yield was >99.9% GVL and was unchanged in the next 8 runs (ESI Fig. S1†, ESI Table S1†, and ESI Pict S4†). The water content of the combined 10 distillates was removed by vacuum distillation (5 Hgmm) using 10 cm of Sulzer EX-20 at 40 °C resulting in 247.5 40 g (2.47 mol) colorless GVL with a water content of 98 ppm and 36.3 g of water. This result showed, that the improved Ru/BDPP

catalyst system was stable enough with the catalyst and ligand amounts and reaction conditions applied here for successful recycling including low-pressure separation step. Since 100% 45 conversion was obtained, it cannot be stated whether the catalyst lose any activity or not during the course of the reactions.²⁶

In order to investigate the applicability of the catalyst for the conversion of LA derived directly from dehydration of carbohydrate, 4 g (22.2 mmol) of D-fructose was dissolved in 80 50 mL of 2 M H₂SO₄ and heated at 170 °C for 8 h.²⁷ After our published workup procedure²⁷ ca. 1.3 mL (1.57 g) of LA was obtained as a dark brownish-yellow solution (ESI Pict S5†). It represents a slightly higher yield of LA than that was obtained for the microwave-assisted dehydration of fructose (400 mg).²⁷ 55 However, humin formation can not be excluded in the acid-catalysed dehydration process as described by Horváth *et al.*¹² In 1 mL of this solution, 6.2 mg of Ru(acac)₃ and 66.5 mg of DPPB was dissolved, then it was transferred to a 10 mL HP Parr reactor. The mixture was pressurized to 100 bar of H₂ and heated to 140 60 °C. By using ¹H-NMR and GC monitoring, it was found that complete conversion was obtained after 1 h (ESI Fig S2† S3†). To summarize, an improved catalyst system was developed and successfully used for the hydrogenation of “real” bio-derived levulinic acid.

65 Experimental

Levulinic acid, 1,2-bis(diphenylphosino)ethane (DPPE), 1,3-bis(diphenylphosino)propane (DPPP), 1,4-bis(diphenylphosino)butane (DPPB), 1,5-bis(diphenylphosino)pentane (DPPPe), 1,6-bis(diphenylphosino)hexane (DPPH), D-fructose, 70 (±)-BINAP were purchased from Sigma-Aldrich and used as received. GC analyses were performed on an Agilent 6890N instrument with HP-Innowax capillary column (15 m x 0.25 μm x 0.25 μm) using He as a carrier gas. For the analysis, 10 μL of reaction mixture was added to 1 mL of methylene chloride 75 followed by the addition of 10 μL toluene as an internal standard.

In a typical hydrogenation experiment, the 30 mL Parr HP reactor was charged with 34.02 g (30 mL, 293.02 mmol) levulinic

acid followed by the addition of Ru(acac)₃ and the corresponding phosphine ligand resulting in a light red solution. The reaction mixture was pressurized to the desired values and heated up to 140 °C. Samples were taken for off-line GC analysis via a dip-leg into a sample holder. After the given reaction time, the autoclave was cooled to ambient temperature and stirring was stopped.

To prepare “real” bio-based levulinic acid, 4 g of D-fructose was dissolved in 80 mL of 2 M H₂SO₄. The solution was transferred into a 120 mL HP Parr HC reactor equipped with PID temperature controller (Parr 4843), safety relief, sampling line and a manometer. When the temperature reached 170 °C, the pressure increased to 18 bar. After 8 h, the mixture was cooled down and the dark brownish-black reaction mixture was filtered on a glass filter. The black solid was washed with 3 × 30 mL of distilled water and with 3 × 30 mL of ethyl acetate. The aqueous phase was separated and extracted with 4 × 100 mL of ethyl acetate. The combined straw-yellow organic phase was dried over MgSO₄. The solvent was removed under reduced pressure at 60 °C resulting in ca. 1.3 mL (1.57 g) dark brown liquid as product. Yield: 51%.

Conclusions

We have demonstrated that the catalyst *in situ* generated from Ru(III)-acetylacetonate and 1,4-bis(diphenylphosphino)butane (DPPB) can be used for the efficient conversion of biomass derived levulinic acid to gamma-valerolactone representing TOF of 21233 h⁻¹. The catalyst can be recycled for ten consecutive runs while full conversion of LA was obtained. The maximum hydrogenation rate was achieved by applying 10-fold excess of DPPB ligand to the Ru precursor.

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