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## Communication

# Catalytic hydrogenation of levulinic acid in aqueous phase

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## ABSTRACT

The hydrogenation of levulinic acid (LA) yielding  $\gamma$ -valerolactone (GVL) has been examined in aqueous solution using various water soluble phosphine ligands in combination with the metal precursors [Ru(acac)<sub>3</sub>] and [RuCl<sub>3</sub>]. Using catalyst loadings of only 0.2 mol%, GVL could be obtained in yields up to 99% conversion and 97% selectivity along with a maximum turnover frequency of 200 mol<sub>GVL</sub> mol<sub>Ru</sub><sup>-1</sup> h<sup>-1</sup> within 5 h, using 3,3',3''-phosphinidynetris(benzenesulfonic acid) trisodium salt (TPPTS) and Ru(acac)<sub>3</sub> as catalytic system. In addition, a ruthenium–phosphine complex immobilized on the amphiphilic copol-ymer PS-PEG was examined under the same conditions and gave 90% conversion of LA in 24 h.

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Chemical feedstock and fuels produced from petroleum seem to have a limited future. The awareness of our planets limited crude oil resources and new ecological sensibility triggered the search for alternative energy and carbon sources based on renewables and CO2 neutral raw materials [1]. Biomass-derived alternatives fulfill these requirements and, in addition, are often nontoxic and biodegradable [2]. A highly promising carbohydrate based sustainable solvent and fuel additive is  $\gamma$ -valerolactone (GVL) due to its favorable properties such as inertness towards oxygen and water, high boiling and flash point, low melting point, low vapor pressure and decent smell [3]. GVL, accessible from agricultural waste, can be converted to (liquid) alkenes, fine chemicals and also used for food additives or energy generation [4–7]. The bulk scale industrial precursor of GVL is 4-oxopentanoic acid or levulinic acid (LA), which is among the twelve most promising biomass-derived building-block chemicals, due to its inexpensive synthesis from wood, starch or glucose [1,8,9].

The hydrogenation of LA or its esters has been reported employing a broad variety of different metal based catalysts and methodologies [10–21], albeit some of the best results leading to GVL were obtained with Ruthenium-based catalysts [6,10,11,18]. While most of these catalytic transformations are carried out in organic solvents such as DCM, acetone or methanol [22–26], reports of more environmentally benign reactions in aqueous media are comparatively rare (Scheme 1). Already in 1977, Joó et al. described the hydrogenation of LA using a ruthenium catalyst under very mild conditions (60 °C, 0.1 MPa), though without mentioning any selectivity [27]. Later, Mehdi et al. reported the reaction using [Ru(acac)<sub>3</sub>] and tri-*n*-butyl phosphine (PBu<sub>3</sub>) as catalyst together with ammonium hexafluorophosphate (NH<sub>4</sub>PF<sub>6</sub>) as additive at 10 MPa and 135 °C, or with [Ru(acac)<sub>3</sub>] and 3,3',3"-phosphinidynetris(benzenesulfonic acid) trisodium salt (TPPTS) at 6.9 MPa and 140 °C in water [5]. Chalid et al. used the same ligand successfully in a biphasic water/DCM system and Serrano-Ruiz et al. reported successful application of a metal based supported catalyst (5% Ru/C)for the hydrogenation of aqueous levulinic acid (50 wt%), at 150 °C and 3.5 MPa under continuous flow conditions [28,29]. Just recently, Tukacs et al. presented catalytic examination of a series of sulfonated phosphane ligands in combination with  $[Ru(acac)_3]$  [18]. In this work, we report a kinetic catalyst screening of Ru complexes with different water-soluble phosphine ligands (Fig. 1), substituted with carboxylic acids, amines or sulfones as homogeneous, immobilized or heterogeneous catalyst systems, in order to identify a simple and straightforward catalyst/ligand combination for the pivotal transformation of levulinic acid to  $\gamma$ -valerolactone.



**Scheme 1.** Aqueous hydrogenation of levulinic acid (LA) into *γ*-valerolactone (GVL).

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**Fig. 1.** Ligands used for the aqueous hydrogenation of levulinic acid to γ-valerolactone: **1**: Tris(2-carboxyethyl) phosphine; **2**: 1,3,5-Triaza-7-phosphaadamantane (PTA); **3**: Tris(2,4-dimethyl-5-sulfophenyl) phosphine trisodium salt (TXTPS); **4**: [2-(dicyclohexylphosphino)ethyl] trimethylammonium chloride; **5**: 3-(diphenylphosphino)benzenesulfonic acid sodium salt (TPPMS); **6**: 3,3',3''-Phosphinidynetris(benzenesulfonic acid) trisodium salt (TPPTS).

In a general synthetic procedure, the substrate (26.4 mmol), the metal precursor, [Ru(acac)<sub>3</sub>] (0.044 mmol), and the ligand (0.44 mmol) (Fig. 1) were introduced in a flask filled with 40 mL of degassed water and stirred until total dissolution. This solution was transferred under argon into the autoclave PTFE insert that was subsequently introduced in the autoclave, which was sealed and flushed with nitrogen for several minutes. The reaction was warmed up to 140 °C at an agitation rate of 1400 rpm. At 140 °C, 5 MPa of hydrogen were introduced into the autoclave. Pressure was maintained through free supply of hydrogen to the reaction vessel. Samples were obtained through the liquid sampling valve each hour for the first 6 h and subsequently after 21 h or 24 h, respectively. The samples were then filtered through filter paper and deep-frozen for later analysis by HPLC. At the end of the reaction, the autoclave was cooled down to 50 °C in a water bath and pressure was released (see Supporting information).

Although LA was reduced to GVL by all examined catalyst systems, significant differences could be detected. Ligands **1** and **2** with less bulky substituents gave poor activities (TOFs <  $20 \text{ mol}_{\text{GVL}} \text{ mol}_{\text{Ru}}^{-1} \text{ h}^{-1}$ ) and even after a reaction time of 21 h no complete conversion could be observed (Table 1). However, the more sterically demanding ligands **3**–**6** gave satisfactory TOFs from 117 to  $202 \text{ mol}_{\text{GVL}} \text{ mol}_{\text{Ru}}^{-1} \text{ h}^{-1}$ . The two phosphine ligands giving the best catalytic results were TPPMS **5** and TPPTS **6**, revealing highest TOFs (194 and 202 mol\_{\text{GVL}} mol\_{\text{Ru}}^{-1} \text{ h}^{-1}, respectively) and conversions (94% and 99%, respectively) after 5 h, combined with high selectivities (94% and 97%, respectively). Employing only 0.02 mol% of the same catalyst system, Tukacs et al. observed 23% yield of GVL within 1.8 h, using a pressure of 10 MPa and otherwise comparable conditions [18].

In order to determine the influence of the ligand,  $[Ru(acac)_3]$  was examined without any phosphine ligands present (entry 7, Table 1). Interestingly, the metal precursor gave a high TOF (570 mol<sub>GVL</sub> mol<sub>Ru</sub><sup>-1</sup> h<sup>-1</sup>). However, fast discoloring of the reaction solution took place and after 1 h black particles were

## Table 1

Hydrogenation of levulinic acid (26.4 mmol) with  $[Ru(acac)_3]$  (0.044 mmol) and ligands **1-6** (0.44 mmol) at 140 °C and 5 MPa H<sub>2</sub> in 40 ml water (general procedure A); for entry 8, 0.044 mmol of supported Ru was used, based on elemental analysis (general procedure B): Turnover frequency (TOF), conversion (X) and selectivity (S) were determined after 5 or 21 h.

N°	Catalyst	TOF, $[mol_{GVL} mol_{Ru}^{-1} h^{-1}]$	After 5 h		After 21 h	
			X, %	S, %	X, %	S, %
1	$[Ru(acac)_3] + 1$	10	1	_	62	39
2	[Ru(acac) <sub>3</sub> ] + <b>2</b>	13	3	100	34	14
3	[Ru(acac) <sub>3</sub> ] + <b>3</b>	117	23	95	26	100
4	$[Ru(acac)_3] + 4$	135	59	100	84	91
5	[Ru(acac) <sub>3</sub> ] + <b>5</b>	194	94	94	100	92
6	[Ru(acac) <sub>3</sub> ] + <b>6</b>	202	99	97	100	92
7	[Ru(acac) <sub>3</sub> ]	569	100	98	N.D <sup>a</sup>	N.D <sup>a</sup>
8	Ru 5% on $Al_2O_3$	575	100	98	100	86

<sup>a</sup> N.D.: not determined.

observable. The decomposition product, most likely Ru clusters, catalyze the hydrogenation of levulinic acid into GVL heterogeneously, with high conversion and selectivity. This observation suggests the conclusion that heterogeneous catalysts are superior to homogeneous systems under the applied reaction conditions.

In order to provide further evidence, an alumina (Al<sub>2</sub>O<sub>3</sub>) supported 5% Ru catalyst, similar to the one reported by Serrano-Ruiz et al., was examined (entry 8, Table 1) [17]. With a TOF of 575 mol<sub>GVL</sub> mol<sub>Ru</sub><sup>-1</sup> h<sup>-1</sup>, the results obtained are even somewhat higher than for [Ru(acac)<sub>3</sub>], further supporting the hypothesis that the active species in the case of [Ru(acac)<sub>3</sub>] are Ru clusters. It should be noted though, that for the reaction with the alumina supported catalyst selectivity to GVL slowly decreases after 3 h (from 99% after 3 h to 86% after 21 h), possibly due to further hydrogenation of GVL into subsequent reduction products.

Given the more convenient product isolation associated with heterogeneous catalyst systems, higher relevance for industrial application and the satisfying results for the hydrogenation of LA to GVL catalyzed by Ru on alumina, supported types of catalysts were studied in more detail, because the question remained, whether better defined heterogeneous catalysts – i.e. immobilized Ruthenium complexes – would yield even more promising results. For this purpose, a catalyst on an amphiphilic polystyrene– polyethylene glycol (PS–PEG) copolymer was chosen, as this kind of support promises good contact to the aqueous reaction solution as well as easy catalyst removal by filtration, [RuCl<sub>2</sub>(PS–PEG-adppp)<sub>2</sub>] **7** (adppp = 2-aza-1,3-bi(diphenyl-phosphino)propane) developed by Kayaki et al. was synthesized (see Fig. 2) [30,31].

Since this compound represents an analogue of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>], both complexes were examined for hydrogenation of levulinic acid to GVL in water under the same conditions. For further comparison, a homogeneous catalyst was also examined, formed in-situ from RuCl<sub>3</sub> and TPPTS ligand **6**. Catalysis results are presented in Table 2.

The homogeneous catalyst system yielded a similar TOF  $(210 \text{ mol}_{GVL} \text{ mol}_{Ru}^{-1} \text{ h}^{-1})$  as the one observed with the same ligand and  $[\text{Ru}(\text{acac})_3]$  as metal precursor  $(202 \text{ mol}_{GVL} \text{ mol}_{Ru}^{-1} \text{ h}^{-1})$ , entry 6 in Table 1). The amount of anionic ligand **6** does not seem to have any impact on the initial TOF. The immobilized material shows lower activity (TOF of 78 mol\_{GVL} mol\_{Ru}^{-1} \text{ h}^{-1}), however, after 24 h, higher conversion was achieved. The non-water-soluble complex  $[\text{RuCl}_2(\text{PPh}_3)_3]$  is associated with a relatively low TOF



**Fig. 2.** Ruthenium complex **7** with two polymer supported phosphine ligands  $[RuCl_2(PS-PEG-adppp)_2]$  (with adppp = 2-aza-1,3-bi(diphenylphosphino) propane).

#### Table 2

Hydrogenation of levulinic acid (158 mmol) with Ru catalyst following general procedure C (0.0158 mmol Ru, calculated by elemental analysis) at 140 °C and 5.5 MPa H<sub>2</sub> in 40 ml water; in entry 11, 6 (0.0513 mmol) was added: Turnover frequency (TOF), conversion (X) and selectivity (S) were determined after 5 or 24 h.

N°	Catalyst	TOF, $mol_{GVL} mol_{Ru}^{-1} h^{-1}$	X after 5 h, %	S after 5 h, %	X after 24 h, %	S after 24 h, %
9	7	78	49	81	97	87
10	[RuCl <sub>3</sub> ] + 6	210	74	91	90	86
11	$[RuCl_2(PPh_3)_3]$	92	22	86	23	97

 $(92 \text{ mol}_{\text{GVL}} \text{ mol}_{\text{Ru}}^{-1} \text{ h}^{-1})$ , and conversion stopped at 23%, exemplifying the necessity of the catalyst's water solubility.

The catalytic activity of the various Ru phosphine systems seems to be highly dependent on the ligand's steric bulk. Lowest TOFs were observed for ligands 1 and 2, but no black particles - indicative of cluster formation - were observed. Given the small cone angles of the ligands (ca  $137^{\circ}$  for **1**, and  $103^{\circ}$  for **2**) [32–34] it is likely that under the examined conditions these ligands form complexes of general composition  $[RuH_2L_4]$  or even  $[RuH_5]^+$ , restricting the space for carbonyl coordination [35,36]. Ligands TPPMS **5** and TPPTS **6** with higher cone angles (151° and 165°, respectively) [37] show higher catalytic activity, which might be explained by the formation of [RuH<sub>2</sub>L<sub>3</sub>(OH<sub>2</sub>)] [35,38]. The higher steric bulk of the ligand facilitates a free site for better substrate coordination in the latter case. Although ligand TXPTS 3 shows significant steric bulk (210°) [39], catalytic activity was modest. Obviously, there is an upper limit of steric congestion, which is already exceeded in this case. Electronic effects appear to be overruled by steric effects, since the comparable electronic properties of 3, 5 and 6 do not account for the detected catalytic disparity [40]. In the cases of **3–6**, complex decomposition was observed, indicated by visible Ru colloids and probably caused by higher steric bulk [41]. Nevertheless, catalytic activity should have improved hereafter, as observed for [Ru(acac)<sub>3</sub>]. The absence of such an increase might be explained by the coordination of abundant phosphine ligands to the Ru clusters.

The lower activity of the immobilized ligand could be explained by higher electron density at the Ru center or by diffusion limitations – further experiments are underway to gain more insights.

In summary, levulinic acid can be reduced to GVL in water at 140 °C and 5 MPa (H<sub>2</sub>) using ruthenium complexes and a wide range of water-soluble phosphines, with a conversion and selectivity of up to 99% and 97% within 5 h - a short reaction time under these comparably mild conditions. A maximal TOF of ca. 200  $\text{mol}_{\text{GVL}} \, \text{mol}_{\text{Ru}}{}^{-1} \, h^{-1}$  could be determined, depending on the steric ligand properties. Nonetheless, highest TOFs  $(>550\ mol_{GVL}\ mol_{Ru}\ ^{-1}\ h^{-1})$  were recorded by less defined heterogeneous catalyst systems, Ru clusters and 5% Ru on alumina. Better defined and more convenient to handle PEG-immobilized catalyst systems led to lower TOFs but higher conversion in comparison to the best homogeneous systems under examination. C.D. and L.A.S. are grateful for generous financial support through TUM Graduate School and Elitenetzwerk Bayern: NANOCAT.

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## Appendix A. Supplementary material data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/i.jorganchem.2012.10.030.

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