Green Chemistry

Cite this: *Green Chem.*, 2012, **14**, 1260

www.rsc.org/greenchem

COMMUNICATION

Exploring the ruthenium catalysed synthesis of γ-valerolactone in alcohols and utilisation of mild solvent-free reaction conditions†

Mohammad G. Al-Shaal, William R. H. Wright and Regina Palkovits*

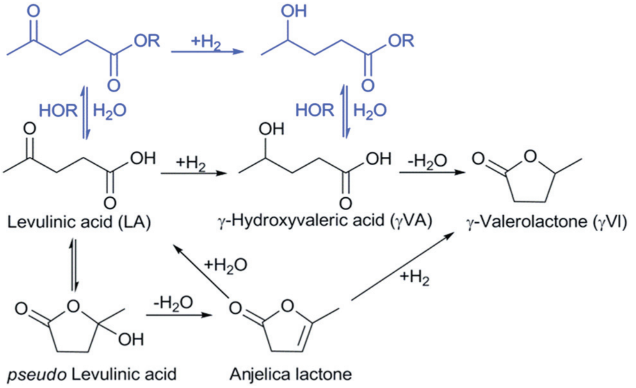
Received 20th December 2011, Accepted 16th February 2012
DOI: 10.1039/c2gc16631c

Levulinic acid and alkyl-levulinates have been hydrogenated using a range of supported catalysts. The different reaction outcomes obtained in alternate solvents have been rationalized and the influence of varying catalyst supports examined. A range of solvent free conditions have been investigated with complete LA conversion obtained at temperatures as low as 25 °C.

Despite numerous difficulties being associated with exploitation of fossil reserves, these resources still form the bases of worldwide fuel and chemical production.[1,2] Ultimately, these finite reserves will be depleted, inevitably forcing a switch to more sustainable feedstocks, such as those obtained from renewable biomass.[3] However, before widespread biomass utilisation can be realised, new processing methodologies must be developed, that are undemanding in energy and close to carbon neutral.[4] This represents a considerable challenge as biomass components (*e.g.* sugars) are typically rich in functionalities, with energy expenditure often required for their conversion to less functionalised more usable compounds.[5] Despite this difficulty, the US DOE has identified key target molecules that can be derived from biomass,[6] including γ-valerolactone (γVl) which may find use as a renewable solvent,[7] fuel additive,[8] or precursor to alkene based transportation fuels.[9] The production of γVl entails the hydrogenation of levulinic acid (LA), a versatile and viable platform chemical that has already been produced efficiently from lignocellulosic biomass on a pilot plant scale.[10,11] Overall, the maximum economic and environmental benefits associated with utilisation of γVl will only be realised if minimal energy is employed during its production. With this in mind, we have re-examined the production of γVl, with the aim of developing less energy demanding 'greener' protocols with lower environmental impact and higher sustainability.

The capacity of a range of bases and precious metals to catalyse LA hydrogenation has already been extensively explored,[12] with the highest γVl yields invariably obtained from Ru-supported catalysts.[12,13] Analysis of hydrogenation reactions using GC-MS has implicated both *pseudo*-LA and γ-hydroxyvaleric acid (γVA) as reaction intermediates (Scheme 1).[13] Notably, the relative favorability of each reaction pathway has not yet been determined, although it has long been established that both *pseudo*-LA and Anjelica Lactone can readily convert back to LA.[14] Furthermore, when alcohols are employed as reaction solvents, both LA and γVA can undergo esterification.[15] However, the overall impact of ester formation on the efficiency of γVl production has not yet been fully explored. This is of interest as the utilisation of small alcohols as a medium for LA hydrogenation could prove to be advantageous, as such solvents arguably have a relatively low net environmental impact and can be derived from biomass.[9,16] Secondly, conversion of lignocellulosic biomass to levulinic esters instead of LA could enable higher yields and easier product separation,[17] suggesting that future γVl production could be based on hydrogenation of levulinic esters.[18]

With the goal of assessing the impact of ester formation upon LA hydrogenation, we have examined the ability of Ru–C to catalyse LA hydrogenation in methanol, ethanol and 1-butanol at 130 °C (Table 1, entries 1–3). As efficient LA hydrogenation has already been demonstrated in 1,4-dioxane,[19] for comparison this solvent was also utilised (Table 1, entry 4). Of the alcohols screened, methanol facilitated the highest γVl yield and selectivity, allowing a similarly high catalyst activity to that obtained using 1,4-dioxane. The conversion of LA in ethanol was notably lower, and significantly worse in 1-butanol, although high selectivities were obtained in all three alcohols (81–85%). To evaluate the extent of ester formation in methanol and 1-butanol, mixtures comprising each alcohol and LA were prepared and heated under



Scheme 1 Reaction pathways for the hydrogenation of LA.

Institut für Technische und Makromolekulare Chemie, RWTH, Aachen University, Worringerweg 1, D-52074 Aachen, Germany. E-mail: palkovits@itmc.rwth-aachen.de

† Electronic supplementary information (ESI) available: Full experimental details alongside supporting charts and tables. See DOI: 10.1039/c2gc16631c

Table 1 LA hydrogenation using supported ruthenium catalysts

	Catalyst[a]	Sub.	Solvent[b]	% LA conv.[c]	% γVl select.[d]	% γVl yield[e]	Moles γVl/gRu[f]
1	Ru–C	LA	Methanol	99.0	85.3	84.4	2.9
2	Ru–C	LA	Ethanol	75.5	81.0	61.1	2.1
3	Ru–C	LA	1-Butanol	48.6	81.7	39.7	1.3
4	Ru–C	LA	1,4-Dioxane	98.8	97.7	95.9	3.3
5	Ru–C	ML[g]	Methanol	97.8	89.4	87.4	3.0
6	Ru–C	BL[h]	Methanol	91.1	82.3	75.1	2.5
7	Ru–C[i]	LA	Methanol	96.4	81.4	78.4	2.6
8	Ru–C[i]	LA	Butanol	100	98.3	98.3	3.3
9	Ru–C	LA	Methanol–H_2O	96.2	87.7	84.5	2.9
10	Ru–C	LA	Ethanol–H_2O	99.2	89.8	89.1	3.0
11	Ru–C	LA	Butanol–H_2O	98.8	76.0	75.1	2.5
12	Ru–C	LA	H_2O	99.5	86.6	86.2	2.9
13	Ru–TiO_2 (T)	LA	Ethanol	0.0	—	—	—
14	Ru–TiO_2(T)	LA	Ethanol–H_2O	0.0	—	—	—
15	Ru–TiO_2(D)	LA	Ethanol	67.7	92.2	62.4	2.1
16	Ru–TiO_2(D)	LA	Ethanol–H_2O	81.2	87.8	71.2	2.4
17	Ru–Al_2O_3	LA	Ethanol	37.7	85.8	32.3	1.1
18	Ru–Al_2O_3	LA	Ethanol–H_2O	94.7	80.4	76.2	2.6
19	Ru–SiO_2	LA	Ethanol	82.9	92.8	77.0	2.6
20	Ru–SiO_2	LA	Ethanol–H_2O	98.0	76.5	74.9	2.5

[a] General conditions: LA (500 mg, 4.31 mmol); Ru (5%) support (25 mg, 0.012 mmols of Ru); Solvent (10 mL); 130 °C; H_2 (12 bar); 160 min; 130 °C. [b] Alcohols of LC-MS grade were purchased from Sigma Aldrich and used as received; with alcohol–water mixtures being generated by mixing 9 mL of an alcohol with 1 mL of water. [c] (Total moles of all products)/(moles LA) × 100. [d] (Moles γVl)/(total moles of all products) × 100. [e] (Moles of γVl)/(moles LA) × 100. [f] (Moles of γVl)/(mass of Ru (g)). [g] ML (560 mg, 4.31 mmol). [h] BL (681 mg, 4.31 mmol). [i] H_2 pressure of 20 bar utilized.

a pressure of H_2 (12 bar, 130 °C, 160 min) in the absence of Ru–C. Analysis of both mixtures at room temperature using ^{1}H NMR spectroscopy demonstrated that the extent of esterification in the methanol and 1-butanol mixtures was 0.5 and 4.0% respectively. To further explore the influence of ester formation on LA hydrogenation, discrete samples of methyl-levulinate (ML) and butyl-levulinate (BL) were both hydrogenated in methanol, utilizing identical conditions to those employed for LA (Table 1, entries 5–6). This resulted in similar conversions and yields to those obtained from LA, establishing that esters of LA can be readily hydrogenated to γVl, and that alkyl-levulinate formation in alcohol solvents does not significantly inhibit γVl production. Thus, while a marginally higher extent of ester formation occurs in 1-butanol, another factor results in the lower γVl yields obtained from this system. Notably, H_2 is more soluble in methanol,‡ with the k_h values for methanol, ethanol and 1-butanol previously reported as being 596, 452 and 358 MPa respectively.[20] Hence, the reduced catalyst activity observed in ethanol and 1-butanol could result from lower concentrations of H_2 in the reaction mixture. In contrast, at increased H_2 pressures (20 bars) we have observed that 1-butanol facilitates higher reaction yields than methanol (Table 1, entries 7–8).

One general means by which the concentration of H_2 can be increased in a given mixture is by the addition of water, which with an associated k_h value of 7500 MPa has a high capacity to dissolve H_2.[21] Thus, adding water to the reaction mixtures could permit high H_2 concentrations, without requiring high pressures and associated engineering costs. With this in mind, mixtures comprised of water (10% by volume) and a given alcohol (90% by volume), were utilized as solvents for LA hydrogenation (Table 1, entries 9–11). For methanol, water addition did not modify γVl production (Table 1, entry 1 *vs.* 9), although using ethanol–water slightly enhanced γVl yield (Table 1, entry 2 *vs.* 10). More noticeably, mixing water and 1-butanol resulted in a substantial increase in LA conversion, without considerable modification of γVl selectivity (Table 1, entry 3 *vs.* 11). Overall, the presence of water can enhance γVl production, which is fortunate as generation of LA *via* hydrolysis of lignocellulosic biomass will result in LA product streams that invariably contain water.[11] To further evaluate the suitability of water as a reaction solvent, LA hydrogenation in pure water was assessed (Table 1, entry 12). This showed that water enables efficient γVl production with notably higher yields obtained than for ethanol or 1-butanol, again indicating that the high k_h value of water can enable higher reaction yields.

The presence of water in LA product streams could create additional challenges with regard to catalyst stability. Consequently, the identification of water tolerant catalysts would be a major factor in facilitating closer process integration and increasing efficiency, by removing the costly need to separate water from LA feeds prior to hydrogenation. Thus, we assessed the capacity of 5 wt% Ru supported on TiO_2 (Tronox), Al_2O_3 and SiO_2, to catalyse LA hydrogenation in ethanol and mixtures of ethanol–water (Table 1, entries 13–20). For Ru–TiO_2 (Tronox) no LA conversion was observed in either ethanol or ethanol–water (Table 1, entries 13–14). In contrast, Ru–TiO_2 (Degussa P25) did initiate γVl production (Table 1, entries 15–16), with the higher specific surface area of this support enhancing catalysis, either by facilitating substrate absorption or enabling a higher Ru dispersion. Overall, the different reaction outcomes rendered by each form of TiO_2 demonstrate that the catalyst support structure can have a profound influence on reaction yields, and further investigations are currently underway to rationalise these effects. Ru–Al_2O_3 was able to catalyze the production of γVl in ethanol, albeit with a low conversion and yield (Table 1, entry 17). Notably, higher catalyst activity was rendered

Table 2 Ruthenium catalysed LA hydrogenation at 25 °C

Catalyst[a]	Reaction time (h)	% LA conver.[b]	% γVA select.[c]	% γVl select.[d]	% γVl yield[e]	Moles γVl/gRu[f]
Ru–C	2.6	10.6	75.7	24.2	2.5	0.08
Ru–C	24	83.7	13.1	86.8	72.7	2.50
Ru–C	40	86.1	7.2	92.7	79.8	2.75
Ru–C	50	100	2.4	97.5	97.5	3.36
Ru–SiO_2	50	2.1	19	81.0	1.7	0.05
Ru–Al_2O_3	50	8.43	24.9	75.1	6.3	0.02

[a] General conditions: LA (5.0 g, 43.1 mmol); Ru(5%) support (250 mg, 0.12 mmols Ru); H_2 (12 bar); Samples of LA acid were initially heated to 35 °C to induce the melting required for catalyst mixing, although, hydrogenation was conducted exclusively at 25 °C. [b] (Total moles of all products)/(moles LA) × 100. [c] (Total moles of γVA)/(moles LA) × 100. [d] (Moles γVl)/(total moles of all products) × 100. [e] (Moles of γVl)/(moles LA) × 100. [f] (Moles of γVl)/(mass of Ru (g)).

by Ru–Al_2O_3 in the ethanol–water mixture, enabling a significantly increased γVl yield (Table 1, entry 18). Similarly, for the Ru–SiO_2 catalyst, a larger γVl yield and catalyst productivity was obtained in the presence of water, although the discrepancy is less noticeable (Table 1, entries 19–20). Overall, these results demonstrate that addition of water to a reaction mixture can enhance the total γVl yields generated by a range of supported Ru catalysts. To assess the relative stability of the reaction products, the Ru–SiO_2 ethanol reaction (Table 1, entry 19) was filtered, stirred at 25 °C for 24 h, and re-analysed using ^1H NMR spectroscopy. The composition of this reaction mixture remained unaltered with the same amount of γVA persisting in solution (7.2%). Evidently, the dehydration of γVA requires elevated temperatures or the presence of a catalyst.

While tolerance of water in LA streams could enable closer process integration, further optimisation of LA hydrogenation, may reduce overall process costs. Total process efficiency could be increased by employing solvent-free conditions that would facilitate the later isolation and processing of γVl derivatives.[22] Thus, we have strived to develop mild solvent-free conditions for the hydrogenation of LA, and have identified that γVl production can be achieved at 25 °C, without the requirement of any additional reaction solvents (Table 2). In our investigations, stirring mixtures of LA, 5 wt% Ru–C under an atmosphere of H_2 (12 bar), resulted in near complete conversion to γVl after 50 h (Table 2). This longer reaction time was necessary as the rate of hydrogenation is considerably diminished at 25 °C. Indeed, the ^1H NMR spectra presented by the reaction mixture after 2.6 h indicated that most of the LA had not been hydrogenated, with γVA identified as the principle reaction product (Table 2). After 24 h, the reaction mixture consisted mainly of γVl, although significant amounts of γVA and LA were present in solution. These components slowly convert to γVl, which after 50 h is contaminated by only trace γVA (2.4%), according to ^1H NMR spectroscopy. Only one previous example of LA hydrogenation at 25 °C has been reported, in which lower LA conversions (87% after 48 h) were rendered by a Pt catalyst.[23] As our previous experiments established that γVA does not readily dehydrate at 25 °C in the absence of a catalyst, in this instance it is probable that this transformation is induced by Ru–C. After 50 h no further modification of the reaction mixture occurred, and the Ru–C was removed from the product mixture by filtration. The Ru–C catalyst was found to be recyclable with marginally better catalyst stability observed at 25 °C than at 130 °C, although direct comparison is certainly not possible due to variations in catalyst productivity at the different reaction conditions (see Chart S1†). Nevertheless, these results indicate that using low reaction temperatures could enable longer catalyst lifetimes, a significant finding as catalyst stability is an important consideration in the development of new sustainable processes.

Of the catalysts screened at 25 °C, Ru–C provided the highest yields (Table 2), with significantly lower activities given by Ru–SiO_2, Ru–Al_2O_3. While dilution of LA with water or γVl markedly decreased Ru–C activity, it was found that this can be mitigated by increasing catalyst loadings (Table S1† entries 1–2). Thus, mixtures of γVl/LA and H_2O–LA were hydrogenated using Ru–C at 25 °C to give γVl yields of 91.4% and 88.8% respectively, with the only other reaction product being γhydroxyvaleric acid (γVA). This demonstrates that LA–H_2O product streams could be hydrogenated at low temperatures and that γVl could be added to reaction mixtures to ensure fluidity. As an alternative to the 50 h reaction times required at 25 °C, we have also found that heating mixtures of LA and Ru–C to 190 °C under an atmosphere of H_2 (12 bar) results in complete conversion of LA to γVl within 40 minutes. Such a system could prove to be highly attractive for technical implementation, with the fast reaction times enabling very high space time yields permitting minimal net energy expenditure. In conclusion, we have established that for many systems solvent selection can have a significant influence on γVl yields with water addition often enhancing γVl production. Furthermore, solvent-free conditions have been demonstrated, both at 25 °C and 190 °C.

Acknowledgements

We wish to thank the Higher Institute of Applied Science and Technology of Syria for the studentship of Mohammad G. Al-Shaal (Grant Number 1596/MT). This work was supported by the Robert Bosch Foundation in the frame of the Robert Bosch Fellowship for the efficient utilization of renewable resources.

Notes and references

‡ The mole fraction of H_2 in a given solution can be determined using Henry's law equation, $p(H_2) = k_h \times c(H_2)$. Where p is H_2 partial pressure and c is H_2 solution concentration.

1 BP, *Statistical review of world energy*, June 2011, bp.com/statisticalreview
2 G. E. Totten, S. R. Westbrook and R. J. Shah, *Fuels and lubricants handbook: technology, properties, performance, and testing*, ASTM International, Glen Burnie, 2003.

3 R. Rinaldi and F. Schűth, *Energy Environ. Sci.*, 2009, **2**, 610; B. Kamm, P. R. Gruberand M. Kamm, *Biorefineries – industrial processes and products*, Wiley-VCH, Weinheim, Germany, 2006, vol 1, p. 15.
4 For an overview relating to biomass processing see; M. Parikka, *Biomass Bioenergy*, 2004, **27**, 613–620; A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, Jr., J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484–489; M. J. Climent, A. Corma and S. Iborra, *Green Chem.*, 2011, **13**, 520–540; J. C. Serrano-Ruiz and J. A. Dumesic, *Energy Environ. Sci.*, 2011, **4**, 83–99; R. Palkovits and M. Rose, *Macromol. Rapid Commun.*, 2011, **32**, 1299–1311.
5 J-ten. Dam and U. Hanefeld, *ChemSusChem*, 2011, **4**, 1017–1034.
6 J. J. Bozell and G. R. Petersen, *Green Chem.*, 2010, **12**, 539–554; T. Werpy and G. Petersen, *Top value added chemicals from biomass – results of screening for potential candidates from sugars and synthesis gas*, U. S. Department of Energy, vol. **1**, 2004, NREL/TP-510-35523.
7 P. G. Jessop, *Green Chem.*, 2011, **13**, 1391–1398.
8 I. T. Horváth, H. Mehdi, V. Fábos, L. Boda and L. T. Mika, *Green Chem.*, 2008, **10**, 238–242.
9 J. C. Serrano-Ruiz, D. J. Braden, R. M. West and J. A. Dumesic, *Appl. Catal., B*, 2010, **100**, 184–189; J. Q. Bond, D. M. Alonso, D. Wang, R. M. West and J. A. Dumesic, *Science*, 2010, **327**, 1110–1114; J. P. Lange, R. Price, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke and H. Gosselink, *Angew. Chem., Int. Ed.*, 2010, **49**, 4479–4483.
10 D. W. Rackemann and W. O. S. Doherty, *Biofuels, Bioprod. Biorefin.*, 2011, **5**, 198–214; R. Palkovits, *Angew. Chem., Int. Ed.*, 2010, **49**, 4336–4338.
11 J. J. Bozell, L. Moens, D. C. Elliott, Y. Wang, G. G. Neuenscwander, S. W. Fitzpatrick, R. J. Bilski and J. L. Jarnefeld, *Resour., Conserv. Recycl.*, 2000, **28**, 227–239.
12 L. E. Manzer, *Appl. Catal., A*, 2004, **272**, 249–256.
13 Z.-p. Yan and L. Lin, *Energy Fuels*, 2009, **23**, 3853–3858.
14 D. P. Langlois and H. Wolff, *J. Am. Chem. Soc.*, 1948, **70**, 2624–2626.
15 C. K. Shu and B. M. Lawrence, *J. Agric. Food Chem.*, 1995, **43**, 782–784.
16 M. F. Demirbas, M. F. Demirbas, M. Balat and H. Balat, *Energy Convers. Manage.*, 2011, **52**, 1815–1828.
17 S. Saravanamurugan and A. Riisager, *Catal. Commun.*, 2012, **17**, 71–75; S. Saravanamurugan, O. N. Van Buu and A. Riisager, *ChemSusChem*, 2011, **4**, 723–726.
18 M. Chia and J. A. Dumesic, *Chem. Commun.*, 2011, **47**, 12233–12235.
19 L. E. Manzer, *Appl. Catal., A*, 2004, **272**, 249–256.
20 M. S. Wainwright, T. Ahn, D. C. Trimm and N. W. Cant, *J. Chem. Eng. Data*, 1987, **32**, 22–24.
21 R. M. Purwanto, R. V. Deshpande and H. Delmas, *J. Chem. Eng. Data*, 1996, **41**, 1414–1417.
22 F. M. A. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer and W. Leitner, *Angew. Chem.*, 2010, **122**, 5642–5646.
23 H. A. Schuette and R. W. Thomas, *J. Am. Chem. Soc.*, 1930, **52**, 3010–3012.