RSC Advances

COMMUNICATION

View Article Online View Journal | View Issue

New generation biofuels: γ-valerolactone into valeric esters in one pot[†]‡

Cite this: RSC Advances, 2013, 3, 1302

Received 23rd November 2012, Accepted 23rd November 2012

pted 23rd November 2012 and reden

DOI: 10.1039/c2ra23043g

www.rsc.org/advances

Ethyl valerate and pentyl valerate, suitable as a gasoline additive and diesel component respectively, can be obtained in a one pot one step reaction from γ -valerolactone, readily available from lignocellulosic biomass. The reaction takes place in ethanol under H₂ through nucleophilic addition of the alcohol to the carboxylic group giving hydroxypentanoate, dehydration to pentenoate and hydrogenation to the saturated ester. The bifunctional catalyst used consists of a non noble metal, namely copper, supported on an amorphous weakly acidic material, therefore representing an interesting alternative to Pt-zeolite catalysts. Pentyl valerate can be obtained in one pot with conversions >90% and selectivity up to 83%.

One of the most promising pathways towards a new bio-based economy is the synthesis of new transportation fuels starting from lignocellulosic raw materials.¹ Most of the transformations involved in this pathway require acidic or hydrogenation catalysts, quite often combined in the same material.²

Several processes to selectively obtain levulinic acid (LA) from a variety of cellulosic raw materials have been reported and one has already reached the commercial scale.³ All of them rely on acid hydrolysis treatments. The hydrogenation of LA gives γ -valerolactone (GVL).⁴

A lot of attention is given to GVL, as it has been identified as a platform molecule with many applications as a precursor for chemicals and fuels.⁵ Among a number of applications, GVL can

Carine E. Chan-Thaw,^a Marcello Marelli,^b Rinaldo Psaro,^a Nicoletta Ravasio*^a and Federica Zaccheria^a

be (a) used directly as a fuel additive,⁶ (b) an environmentally benign solvent,⁷ (c) hydrogenated to form 1,4-pentandiol,⁸ which readily undergoes dehydration to form methyl tetrahydrofuran, (d) converted to methyl pentenoate⁹ using strong acid catalysts, which can be further converted to nylon intermediates such as adipic acid, dimethyl adipate or caprolactam, (e) converted to ethyl valerate (EV), which is suitable as a gasoline additive at levels of 10% and 20% by volume^{1b} or for fragrance and flavouring applications.

The transformation of GVL into EV in two steps has been reported by Lange *et al.*¹⁰ They used a Pt–ZSM-5 catalyst for the hydrogenation of GVL to valeric acid (VA) and an acidic ionexchange resin for the esterification step. However, they also found that Pt supported on a less acidic SiO_2 –Al₂O₃ material was less selective but more stable than the Pt–zeolite one. These authors also reported some options for process intensification, namely the single step conversion of LA to a mixture of VA and EV as well as the conversion of GVL to mixtures of pentyl valerate (PV) and VA.

Although several processes for the conversion of GVL to valeric or pentenoic acid have been set up,¹¹ to the best of our knowledge the direct transesterification and hydrogenation of GVL to EV or PV has not been reported yet.

In the present paper, we wish to report that a catalyst obtained by deposition of a non noble metal such as Cu onto an amorphous weakly acidic material can be effectively used in the one pot one step transformation of GVL into valeric esters.

We have already reported on the use of amorphous silica zirconia and silica alumina mixed oxides as effective solid acids. Different silicas modified with alumina, and to a lesser extent silica modified with zirconia, were found to be very active in the intramolecular *ene* reaction of citronellal to isopulegol¹² and in the isomerization of α -pinene oxide, giving a product distribution typical of Lewis acids.¹³ On the other hand silica modified with a very low loading of ZrO₂ (1 to 5%) is very active in the aminolysis of styrene oxide in toluene, in agreement with the presence of Lewis acid sites highlighted by two bands at 1448 and 1609 cm⁻¹ resistant up to 250 °C in the IR spectrum of adsorbed pyridine.¹⁴

^aISTM-C.N.R., via G. Venezian 21, I-20133 Milano, Italy.

E-mail: n.ravasio@istm.cnr.it; Fax: + 39 02 50314405; Tel: + 39 02 50314382 ^bISTM-C.N.R., via Fantoli 15/16, I-20138 Milano, Italy

 $[\]dagger$ Electronic supplementary information (ESI) available: detailed synthesis, recycling test, ICP, H2-TPR, XRD and TEM and STEM micrographs. See DOI: 10.1039/ c2ra23043g

[‡] **Experimental Section**: hydrogenation reactions were carried out in a high pressure stainless steel Parr 4560 autoclave (100 mL) equipped with a P.I.D controller 4848. Typical conditions consisted of an EtOH–GVL molar ratio of 10, a GVL–catalyst weight ratio of 10, with a reactor operating at 250 °C and 10 bar of H₂ for 20 h under 700 rpm stirring. Catalysts and reactants were poured into the autoclave which was then sealed, evacuated and then loaded with 10 bar H₂. After reaction, the autoclave was cooled down and the mixture was filtrated and analyzed by HPLC, NMR, GC-MS and GC/FID.

The same materials, and particularly a 4.7% zirconia on silica (SiZr 4.7), were also found to be effective catalysts in the esterification of fatty acids with methanol.¹⁵ In this reaction SiZr 4.7 is able to convert 91% of tall oil, a mixture of free fatty acids, in 1 h at 180 °C, showing remarkable resistance to the water formed during reaction, in sharp contrast with other solid acid catalysts that require temperatures ≥ 200 °C or the *in situ* removal of water to reach acceptable conversions.¹⁶ Excellent results were also obtained over these solid amorphous materials in the esterification of oleic acid with TMP.¹⁷

We also succeeded several times in combining the acidic properties of these solids with the hydrogenation activity of prereduced CuO, both for the one step synthesis of ethers starting from ketones^{18,19} and for the esterification and simultaneous hydrogenation of tall oil. In this case, the presence of Lewis acid sites was evident in the spectrum of adsorbed pyridine also after deposition of the CuO phase on the acidic support.²⁰

Therefore we applied the same strategy to the one pot ring opening and hydrogenation of GVL.

Selected results obtained in the transesterification of GVL to EV are reported in Table 1. Catalysts with the same Cu loading (8% by weight), prepared by the same technique on different supports were investigated in order to compare the total conversion and the selectivity to EV at 250 $^{\circ}$ C and 10 bar H₂. The four supports were amorphous silica alumina, zeolite ZSM-5, two amorphous silica zirconia mixed oxides with comparable Zr contents and different textural properties.

All the catalysts supported over amorphous materials gave good results in terms of conversion under the chosen conditions. Over both Cu–SiZr systems EV, 4-hydroxy ethyl pentanoate 1 and ethyl 4-ethoxy pentanoate 2 accounted for 97% of the reaction products. Besides EV, the product of interest, the quantity of ethyl 4-ethoxy pentanoate was not negligible (Scheme 1). The latter was recently prepared from GVL and shown to be a valuable biooxygenated solvent with a vapour pressure higher than GVL but much lower than methyl *tert*-butyl ether (MTBE) and ethyl *tert*butyl ether (ETBE), commonly used as octane boosters.²¹

Formation of both products can take place through the same intermediate 4-hydroxy-ethylvalerate (identity confirmed by NMR, ESI†), which is formed by the nucleophilic addition of ethanol to the carbonyl group of GVL. A blank experiment confirms that 4-hydroxy-ethylvalerate **1** is the major product in the absence of a catalyst.

Table 1 Conversion of GVL to ethyl valerate, 4-hydroxy ethyl pentanoate and ethyl 4-ethoxypentanoate

	Conv. (%)	Sel EV (%)	Sel 1 (%)	Sel 2 (%)	Sel 3 (%)
8% Cu–SiZr A ^a	77	37	4	56	_
8% Cu–SiZr B^b	69	59	7	31	_
5% Cu-SiZr B	67	44	2	36	18
8% Cu–SiAl	77	32	5	39	22
8% Cu-ZSM-5	54	14	4	7	_
Blank	6	5	65	23	

^{*a*} 4 wt.% ZrO₂. ^{*b*} 4.7 wt.% ZrO₂. Run conditions: 250 °C, 10 bar H₂, 700 rpm, 20 h, GVL–catalyst = 10 : 1 wt., GVL–EtOH = 1 : 10 mol.

View Article Online



Scheme 1 Proposed mechanism for the conversion of GVL to 4-hydroxy ethyl pentanoate, ethyl pentanoate (ethyl valerate) and ethyl 4-ethoxy pentanoate.

The addition of methanol to GVL giving the analogous hydroxyl ester followed by dehydration to methylpentenoate has also been reported by the group at Shell under catalytic distillation conditions.^{9b}

The difference in product distribution among the two SiZr based catalysts may be due to different distribution of weak and medium strength acidic sites,²² as already evidenced in the esterification of fatty acids.¹⁵ The method used for the preparation of these copper catalysts leads to the formation of a highly dispersed metallic phase with an outstanding hydrogenation activity for a wide range of supports, as clearly shown for TiO₂, SiO₂ and silica–titania systems.²³

The poor activity of conventional Cu catalysts such as copper chromites in hydrogenation reactions is the reason why they are seldom encountered in biomass transformation reactions where Ni and Ru play a major role.²⁴

On the surface of the Cu–SiZr B system, Cu particles are well shaped and crystalline (Fig. 1) and the synergy with a weakly acidic surface can account for the formation of EV in the present reaction. Thus, hydroxyl-pentanoate can be readily dehydrated over the acidic surface to ethylpentenoate 3, which under these reaction conditions will be hydrogenated to EV. This reaction pathway was confirmed by the comparison with a catalyst supported on silica–alumina. In this case, besides the other products, 22% ethyl pentenoate 3 was formed, in agreement with the poor reducibility of the Cu phase on this support. Thus, the



Fig. 1 TEM image (A) and HRTEM (B) of the fresh Cu–SiZr B catalyst showing the presence of crystalline planes.

number of strong acid sites of this silica–alumina material determined by adsorption calorimetry is close to that determined for a H-beta zeolite sample.²⁵ The exchange with the $Cu(NH_3)_4^{2+}$ solution then generates an isolated copper species, hardly reducible to the metallic state,²⁶ and therefore the Cu–SiAl material shows a very poor hydrogenation activity.²⁷

Very similar results were obtained over a 5% Cu–SiZr catalyst that shows a much lower hydrogenation activity. Previous work showed that the size of the metallic particles in catalysts prepared by the chemisorption hydrolysis technique does not change very much going from 5 to 8% loading,^{23b} whereas the hydrogenation activity increases according to the higher Cu content.²⁸ On the other hand, the catalyst obtained using a zeolite support gave a messy product distribution where the desired product was present in a low amount.

The good results obtained with Cu–SiZr B prompted us to carry out some stability tests on this catalyst. (Table S1, ESI†). After each run, the reactor was cooled down to room temperature, and emptied of the remaining gas. The liquid part was easily separated from the catalyst and the new mixture of GVL–EtOH was loaded into the reactor and brought to 10 atm H₂ before heating to 250 °C. Once this temperature was reached, the mixture GVL–EtOH and catalyst was stirred for 20 h.

The catalyst was pre-reduced in H_2 before the first run to allow formation of the Cu(0) phase, active in the hydrogenation step, in the absence of reagents (see TPR profile S1, ESI†). However no reactivation was needed before the following 8 runs showing that after the reaction either the catalyst is still present in its reduced form or in a form easily reducible under reaction conditions (10 bar H_2).

Along the nine runs, a slight deactivation was observed. However, the yield of EV was kept constant up to the 5th one (Fig. 2, Table S1, ESI[†]) with an average productivity of 25.4 mmol g_{Cu}^{-1} h⁻¹. This slight loss of activity can be explained by some possible removal of the catalyst during the separation of the reagent from the catalyst for the recycling test, by some Cu leaching (Table S2, ESI[†]) but in particular by some changes in the particle size distribution clearly shown by TEM analysis.

80 70 % Conversion % / -=- Yield_{Ev} 60 50 40 30 20 10 ٥ R2 R1 R3 R4 R5 R6 R7 **R**8 R9 Number of runs

Fig. 2 Conversion on recycling 8 wt.% Cu on SiO₂–ZrO₂ B at 250 $^{\circ}$ C and 10 bar H₂, 700 rpm, 20 h. GVL–catalyst = 10 : 1 wt., GVL–EtOH = 1 : 10 mol.

TEM and STEM micrographs (Fig. S2–S4, ESI†), and related size distributions (Fig. 3), show that the particles reorganize and resize along the 9 catalytic cycles. The size of the crystalline Cu NPs for the fresh catalyst (Fig. 1), was mostly centered around 3.7 nm but a marked tail descended up to 18 nm (Fig. 3A). After the first catalytic cycle, the size distribution showed the formation of large aggregates that enlarge the size range up to 50 nm (Fig. 3B). Additional cycles shape and consolidate the distribution to a dual peak mode: the particle size is mostly centered around 3.9 nm but the range is rather large up to 65 nm and the bigger particles were centered around 26.7 nm (Fig. 3C). Reorganization seems to stabilize all the copper aggregates to bigger and more stable crystalline particles along the cycles.

These encouraging results and the insights into the mechanism we draw from them prompted us to investigate the reaction of GVL with PA under hydrogenation conditions. PV was found to be a promising diesel component, showing better volatility and cold flow properties than fatty acid methyl esters. Its synthesis was carried out in one step from GVL through hydrogenation at 275– 300 °C with 20–50% selectivity.¹⁰

Results obtained over Cu–SiZr B, summed up in Table 2, show that when the reaction was carried out under the same experimental conditions reported for the reaction with ethanol, we obtained a sharp increase in conversion jumping from 69 to 93% with an increase in productivity up to 34.3 mmol $g_{Cu}^{-1} h^{-1}$. This can be due to the higher nucleophilicity of pentyl alcohol with respect to ethanol. On the other hand, the selectivity to PV was close to the one obtained with ethanol while the amount of hydroxyvalerate was higher (12%). This suggests that the mechanism of formation is the same, namely ring opening followed by dehydration and hydrogenation.



Fig. 3 TEM micrographs and related size distribution plots (A) Cu–SiZr before reaction (B) Cu–SiZr R1 after the first catalytic run (C) Cu–SiZr R9 after the 9th catalytic run (500 particles).

 Table 2 Conversion of GVL to pentyl valerate and pentyl 4-penthoxypentanoate

_	Conv. (%)	Sel PV (%)	Sel _{pentyl 4-penthoxypentanoate} (%)			
8% Cu–SiZr B	93	59	21			
8% Cu-SiZr B ^a	92	72	16			
,,	91	77	18			
,,	92	81	17			
,,	90	83	14			
Run conditions: 250 °C, 10 bar H ₂ , 700 rpm, 20 h, GVL–catalyst =						
10 : 1 wt., GVL–PA = 1 : 10 mol. ^{<i>a</i>} GVL–PA = 1 : 5 mol.						

The formation of pentenoic or valeric acids can not be excluded. However, under these conditions they would be readily esterified as shown by a separate test (Scheme 2).

To increase the selectivity to PV we lowered the GVL–PA ratio to 1:5 mol. In this way, the chance of forming pentyl-ethers is strongly reduced.

Analysis of the recycle tests for the reaction with ethanol (Table S1, ESI[†]) had shown that the selectivity to EV gradually increased with reuse of the catalyst. Therefore, some recycle tests were carried out also for the GVL to PV system. A small but definite increase in selectivity was observed, reaching 83% in the fourth cycle, while keeping very good conversions, thus allowing the productivity to reach 47.7 mmol g_{Cu}^{-1} h⁻¹ in the 4th run. A similar increase in selectivity with time on stream was observed in the hydrogenation of GVL to VA at 250 °C and 10 bar over Pt and Pt–Pd supported on amorphous silica alumina.²⁹

It should be underlined that this reaction has never been reported in the literature, therefore comparisons are difficult. Recently, excellent conversion and selectivity have been reported in the ring opening and hydrogenation of GVL to pentanoic acid over a Ce promoted 1% Pd–Nb catalyst³⁰ at 325 °C and 34 bar H₂ and over 5% Pd–Nb₂O₅ under milder conditions (275 °C and 14 bar H₂).³¹ In these reactions the selectivity to pentyl-valerate never exceeded 1%.

As already mentioned, the one pot transformation of GVL to PV has been carried out only by direct hydrogenation of GVL to pentanoic acid and esterification with *n*-pentyl alcohol formed *in situ* through over-reduction of the acid.

Conversions comparable with those obtained in the present work were obtained only in the presence of 0.1% Pd–TiO₂ at 275 °C (95%) or 300 °C (100%) or 1% Pt–TiO₂ at 300 °C (96%) after 10–14 h time on stream.³² However, the selectivity to PV never exceeded 27%.



Scheme 2 Esterification of valeric acid into pentylvalerate over Cu-SiZr B.

The reaction we are presenting here requires the use of pentanol, readily obtainable from biomass, but allows one to obtain up to 72% yield in PV.

Moreover, the catalyst concept is quite new, involving a low activity hydrogenation catalyst and a weakly acidic amorphous material. Therefore, this reaction appears to be a valuable option for process intensification in the multistep pathway from cellulose to new generation biofuels.

Acknowledgements

Pasquale Illiano is kindly acknowledged for performing and analyzing the NMR results. The authors thank the Italian MIUR and Regione Lombardia for financial support through the Projects "Ital-NanoNet" (prot. no. RBPR05JH2P) and "VeLiCa" (no. 14840/RCC) respectively.

References

- (a) 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; (b) J. J. Bozell, *Science*, 2010, **329**, 522.
- 2 (a) J. A. Melero, J. Iglesias and A. Garcia, *Energy Environ. Sci.*, 2012, 5, 7393–7420; (b) K. Shimizu and A. Satsuma, *Energy Environ. Sci.*, 2011, 4, 3140–3153; (c) M. Hara, *Energy Environ. Sci.*, 2010, 3, 601–607.
- 3 (*a*) J. A. Geboers, S. Van de Vyver, R. Ooms, B. Op de Beeck, P. A. Jacobs and B. F. Sels, *Catal. Sci. Technol.*, 2011, 1, 714; (*b*) http://www.carbolea.ul.ie/files/HFHR_Chapter%204_FINAL.pdf; (*c*) http://www.biofuelstp.eu/catalysis_hydrocarbons.html.
- 4 D. J. Braden, C. A. Henao, J. Heltzel, C. C. Maravelias and J. A. Dumesic, *Green Chem.*, 2011, 13, 1755.
- 5 (a) J. Q. Bond, D. M. Alonso, R. M. West and J. A. Dumesic, Langmuir, 2010, 26(21), 16291; (b) J. C. Serrano-Ruiz and J. A. Dumesic, Energy Environ. Sci., 2011, 4, 83–99.
- 6 I. T. Horvath, H. Mehdi, V. Fabos, L. Boda and L. T. Mika, *Green Chem.*, 2008, **10**, 238.
- 7 I. T. Horvath, Green Chem., 2008, 10, 1024.
- 8 H. Mehdi, V. Fabos, R. Tuba, A. Bodor, L. T. Mika and I. T. Horvath, *Top. Catal.*, 2008, 48, 49.
- 9 (a) R. Fischer and U. Vagi (BASF), US Pat., 4, 740, 613, 1998; (b) J.
 P. Lange, J. Z. Vestering and R. J. Haan, Chem. Commun., 2007, 3488.
- 10 J.-P. Lange, R. Price, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke and H. Gosselink, *Angew. Chem., Int. Ed.*, 2010, **49**, 4479.
- 11 (a) J. Q. Bond, D. M. Alonso, D. Wang, R. M. West and J. A. Dumesic, *Science*, 2010, 327, 1110; (b) O. H. Werner and D. W. Darrell (Mobil Oil Corp.) GB 1240580 (A) 1971.
- 12 N. Ravasio, M. Antenori, F. Babudri and M. Gargano, *Stud. Surf. Sci. Catal.*, 1997, **108**, 625.
- 13 N. Ravasio, F. Zaccheria, M. Guidotti and R. Psaro, *Top. Catal.*, 2004, 27, 157.
- 14 F. Santoro, F. Zaccheria, N. I. Shaik and N. Ravasio, *Top. Catal.*, 2012, 55, 606.
- 15 (a) F. Zaccheria, S. Brini, R. Psaro, N. Scotti and N. Ravasio, *ChemSusChem*, 2009, 2, 535; (b) R. Psaro, M. N. Ravasio and F. Zaccheria (CNR), PCT/EP2008/062255, 2008 WO 2009037226 A1.

- 16 (a) K. Suwannakarn, E. Lotero, K. Ngaosuwan and J. G. Foodwin, *Ind. Eng.Chem. Res.*, 2009, 48, 2810; (b)
 P. Mongkolbovornkij, V. Champreda, W. Sutthisripok and N. Laosiripojana, *Fuel Process. Technol.*, 2010, 91, 1510.
- 17 S. Brini, R. Psaro, F. Zaccheria and M. N. Ravasio (CNR), *It. Patent*, Appl. MI2012A001189, 2012.
- 18 N. Ravasio, V. Leo, F. Babudri and M. Gargano, *Tetrahedron Lett.*, 1997, 38, 7103.
- 19 F. Zaccheria, R. Psaro and N. Ravasio, *Tetrahedron Lett.*, 2009, 50, 5221.
- 20 F. Zaccheria, N. Ravasio, C. E. Chan-Thaw, N. Scotti and P. Bondioli, *Top. Catal.*, 2012, **55**, 631.
- 21 D. Fegyverneki, L. Orha, G. Láng and I. T. Horváth, *Tetrahedron*, 2010, **66**, 1078.
- 22 P. Berteau, B. Delmon, J.-L. Dallons and A. Van Gysel, *Appl. Catal.*, 1991, **70**, 307.
- 23 (a) F. Boccuzzi, S. Coluccia, G. Martra and N. Ravasio, J. Catal., 1999, 184(2), 316; (b) F. Boccuzzi, A. Chiorino, M. Gargano and N. Ravasio, J. Catal., 1997, 165, 140.

- 24 A. M. Ruppert, K. Weinberg and R. Palkovits, *Angew. Chem., Int. Ed.*, 2012, **51**, 2564.
- 25 B. Dragoi, A. Gervasini, E. Dumitriu and A. Auroux, *Thermochim. Acta*, 2004, **420**, 127.
- 26 A. Gervasini, M. Manzoli, G. Martra, A. Ponti, N. Ravasio, L. Sordelli and F. Zaccheria, J. Phys. Chem. B, 2006, 110, 7851.
- 27 N. Scotti, D. Monticelli and F. Zaccheria, *Inorg. Chim. Acta*, 2012, 380, 194.
- 28 F. Zaccheria, N. Ravasio, A. Fusi, M. Rodondi and R. Psaro, *Adv. Synth. Catal.*, 2005, **347**, 1267.
- 29 R. J. Haan and J.-P. Lange (Shell Int. Res. B.V.), WO 2011/ 015643 A1.
- 30 R. Buitrago-Sierra, J. C. Serrano-Ruiz, F. Rodríguez-Reinoso, A. Sepúlveda-Escribano and J. A. Dumesic, *Green Chem.*, 2012, 14, 3318.
- 31 J. C. Serrano-Ruiz, D. J. Braden, R. M. West and J. A. Dumesic, *Appl. Catal.*, B, 2010, **100**, 184.
- 32 R. J. Haan and J.-P. Lange (Shell Int. Res. B.V.), PCT/EP2010/ 055862, 2010, WO 2011/015385 A1.