Catalytic upgrading of levulinic acid to 5-nonanone†

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Received 13th November 2009, Accepted 6th January 2010
First published as an Advance Article on the web 27th January 2010
DOI: 10.1039/b923907c

Aqueous solutions of levulinic acid can be catalytically processed, through the intermediate formation of γ-valerolactone (GVL), to an organic liquid stream that spontaneously separates from water, and is enriched in pentanoic acid and 5-nonanone. This organic layer can serve as a source of chemicals or can be upgraded to hydrocarbon fuels.

Petroleum, currently the main raw material for the production of fuels and chemicals, is a non-renewable resource in diminishing supply,[1] the consumption of which leads to accumulation of atmospheric CO_2, a greenhouse gas. These issues have stimulated the search for alternative fuels and chemical feedstocks. In this respect, biomass, being renewable, has been proposed to be an important source of energy and organic carbon for our industrial society,[2] and significant efforts are being made to develop processes that allow the conversion of biomass and biomass-derived products into liquid fuels and chemicals.[3–7]

In the same manner that the petrochemical industry can be essentially constructed from a few building blocks,[8] a recent study has identified (by screening of around 300 substances) 12 promising biomass derivatives based on, among other aspects, their production costs and the potential of these molecules to serve as building blocks for the development of bio-refinery processes.[9] Levulinic acid (LA, 4-oxopentanoic acid) occupies a prominent place in this list because it can be obtained inexpensively and in high yields *via* acid hydrolysis of waste cellulosic materials (*e.g.*, paper mill sludge, urban waste paper, agricultural residues).[10] Additionally, levulinic acid has the potential to serve as a platform chemical for the production of a wide range of value-added compounds such as fuel additives,[11] monomers for plastics and textiles,[12,13] and chemicals.[14]

Levulinic acid, as is common for all the biomass derivatives, suffers from an excess of functionality that makes it difficult to control its reactivity and direct the conversion to targeted compounds. Consequently, one efficient strategy to catalytically convert these resources is based on an initial reduction of the oxygen content in the molecule, leading to the production of less-reactive intermediates that can be subsequently upgraded to the desired products.[5] This approach, which leads to better control of reactivity, has been recently applied to lactic acid (2-hydroxypropanoic acid), a prototypical over-functionalized biomass-derived molecule, using a water-stable bifunctional $Pt(0.1\%)/Nb_2O_5$ catalyst.[15] In this case, by combining dehydration/hydrogenation (to reduce the oxygen content) and C–C coupling reactions (to upgrade reactive intermediates), it is possible to transform, in a single reactor, concentrated aqueous solutions of lactic acid into an organic phase, that spontaneously separates from water and is rich in ketones in the C_4–C_7 range.[16] Following the same approach, we detail herein a catalytic strategy (including dehydration/hydrogenation and C–C coupling reactions, Fig. 1) to upgrade concentrated aqueous solutions of levulinic acid into a set of valuable chemicals and fuels using a limited number of reaction and separation steps.

It is known in the literature that levulinic acid, in the presence of strong mineral or solid acids, dehydrates at moderate temperatures (573–623 K) yielding the corresponding cyclic product, α-angelica lactone (AL, Fig. 1).[17] This substance polymerizes over acidic surfaces,[14] and we observed that upgrading routes involving this intermediate over acidic catalysts typically lead to deactivation of the catalyst and/or loss of carbon. Consequently, we have employed an alternative path, depicted in Fig. 1, to initiate catalytic conversion through the formation of the saturated lactone, γ-valerolactone (GVL), which is water-soluble and more stable than the unsaturated lactone.[18] Thus, by operating at lower temperatures (423 K) over a metal catalyst without the presence of acidic sites (Ru/C), concentrated aqueous solutions of levulinic acid were almost quantitatively converted to GVL (Table 1, entry 1) through the intermediate 4-hydroxypentanoic acid (Fig. 1), the presence of which was confirmed by GC-MS analysis. The catalytic reduction of levulinic acid to GVL has been previously carried out with high yields at high H_2 pressures (100 bar) and low levulinic acid concentrations (7 wt%)[19] or using solvents other than water.[13] We note that, in our case, nearly quantitative GVL yields can also be achieved for concentrated aqueous solutions of LA (50 wt%) at milder conditions (35 bar). The Ru/C catalyst showed high activity for the processing of concentrated solutions of LA, making it necessary to operate at high space velocities (WHSV = 32 h^{-1}) to decrease the conversion below 100% to check for catalyst stability. At these conditions, the catalyst showed slow deactivation with time on stream (from 90 to 68% conversion after 106 h), and treatment of the catalyst under flowing H_2 at 673 K for 2 h allowed for partial recovery of the initial catalytic activity (83% conversion).

Aqueous solutions of GVL can be converted to pentanoic acid (PA, Fig. 1), by means of combined ring-opening (on acid sites) and hydrogenation reactions (on metal sites), over a water-stable bifunctional Pd/Nb_2O_5 catalyst at moderate temperatures and pressures (Table 1, entries 2–6). This transformation has

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† Electronic supplementary information (ESI) available: Catalyst preparation, reaction kinetics studies, acknowledgements. See DOI: 10.1039/b923907c

Table 1 Carbon distributions and carbon selectivities for levulinic acid and GVL conversion over different catalysts

				C distribution (%)[a]			C selectivity (%)[b]					
Entry	Catalyst	Feed	T/K, P/bar, WHSV/h^{-1}	Aq.	Org.	Gas	GVL	PA	C_9=O	CO_x	C_4+C_5 alkanes	C_6–C_7 ketones
1	Ru(5%)/C	50 wt% LA[c]	423, 35, 4.8	100	—	—	96[d]	—	—	—	—	—
2	Pd(1%)/Nb_2O_5	50 wt% GVL[c]	598, 35, 1.2[e]	—	37	63	—	—	—	13	83[f]	—
3	Pd(1%)/Nb_2O_5	50 wt% GVL[c]	598, 35, 1.2[g]	—	72	28	—	54[h]	2	6	35	—
4	Pd(0.1%)/Nb_2O_5	50 wt% GVL[c]	598, 35, 1.2[e]	—	79	21	—	65	3	6	22	—
5	Pd(0.1%)/Nb_2O_5	50 wt% GVL[c]	598, 35, 1.2[g]	—	95	5	—	92	—	1	5	—
6	Pd(0.1%)/Nb_2O_5	50 wt% GVL[c]	623, 35, 0.1[g]	—	81	19	—	6	57[i]	12	6	7
7	$Ce_{0.5}Zr_{0.5}O_2$	Pure PA	698, 20, 1.1	—	86	14	—	1	82	11	3	3
8	$Ce_{0.5}Zr_{0.5}O_2$	Organic layer from entry 5	698, 20, 1.1	—	91	9	—	—	84	8	1	6

[a] Percentage C distribution for a phase i is calculated as (moles of carbon detected in phase i divided by the sum of moles of carbon detected in the three phases) × 100. [b] Percentage C selectivity for a product i is expressed as (moles of carbon as product i divided by the sum of moles of carbon for all the detected products) × 100. C_9=O: 5-nonanone; CO_x: CO and CO_2; C_4: n-butane; C_5: n-pentane; C_6–C_7 ketones: 2-hexanone and 3-heptanone. [c] Aqueous solutions. [d] 4-Hydroxypentanoic acid (3%) and 1,4-pentanediol (1%) accounted for the rest of carbon. [e] H_2 co-feed at 100 sccm. [f] Methane (4%) accounted for rest of carbon. [g] H_2 at 25 sccm and He at 25 sccm co-feed. [h] Nonane (1%) and 1-pentyl pentanoate (2%) accounted for rest of carbon. [i] Nonane (7%) and unidentified products (5%) accounted for rest of carbon.

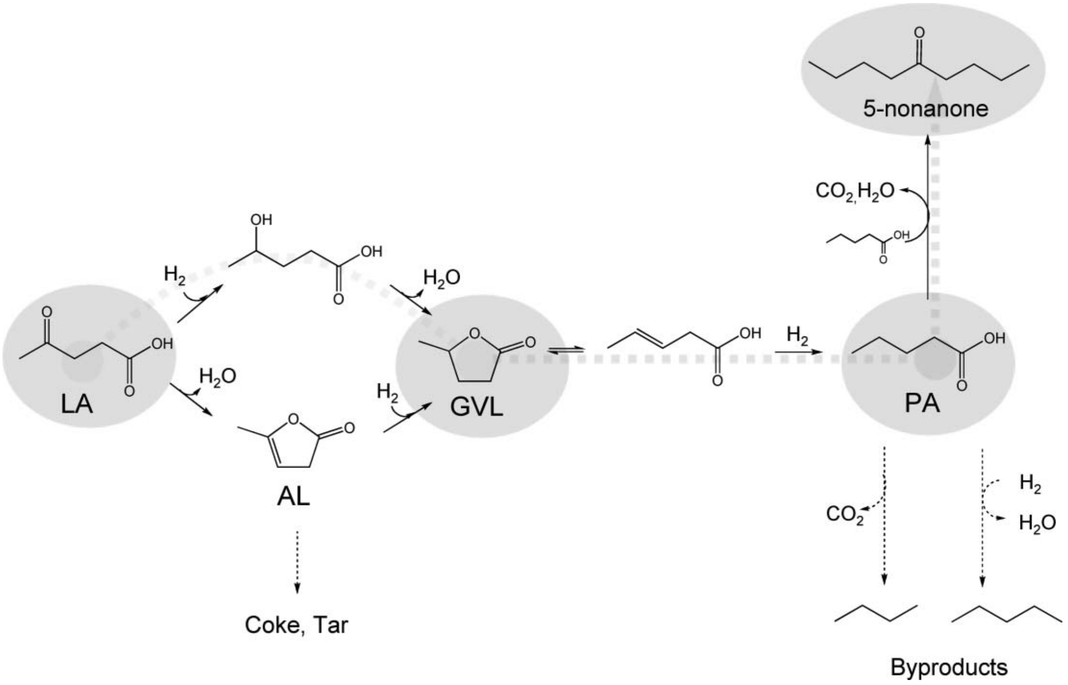

Fig. 1 Catalytic approach used to upgrade levulinic acid by dehydration/hydrogenation and C–C coupling reactions.

previously been described by Ayoub and Lange[14] over a variety of bifunctional metal–acid catalysts. However, as depicted in Fig. 1, production of the desired pentanoic acid is accompanied by the formation of n-butane (produced by decarboxylation of pentanoic acid over metal sites,[20] with the release of stoichometric amounts of CO_x), along with n-pentane (as a result of successive hydrogenations and dehydrations of pentanoic acid over metal and acid sites, respectively). The formation of these unwanted products and the yield to pentanoic acid were found to be controlled by varying the metal loading of the catalyst. Thus, while a Pd(1%)/Nb_2O_5 catalyst converted concentrated aqueous solutions of GVL into a mixture of C_4–C_5 alkanes, CO and CO_2 at 598 K and 35 bar (Table 1, entry 2), a decrease in the metal content by a factor of 10 caused a significant increase in the pentanoic acid yield (from 0 to 65%) at the same conditions of temperature and pressure (Table 1, entry 4). Importantly, owing to its low solubility in water,[21] pentanoic acid was obtained in the separator at the effluent of the reactor, as an organic layer that spontaneously separated from water and accounted for almost 80% of the reacted carbon (see Table 1, entry 4). This liquid organic oil was enriched in pentanoic acid, with minor amounts butane and pentane dissolved in the liquid at the high system pressure. A decrease in the hydrogen partial pressure in the reactor also favored the formation of pentanoic acid *versus* hydrogenation and decarboxylation products (Table 1, entries 3 and 5). Therefore, proper choice of metal catalyst and reaction conditions leads to a yield of pentanoic acid equal to 92%, with 95% of the carbon being stored in the organic layer (Table 1, entry 5).

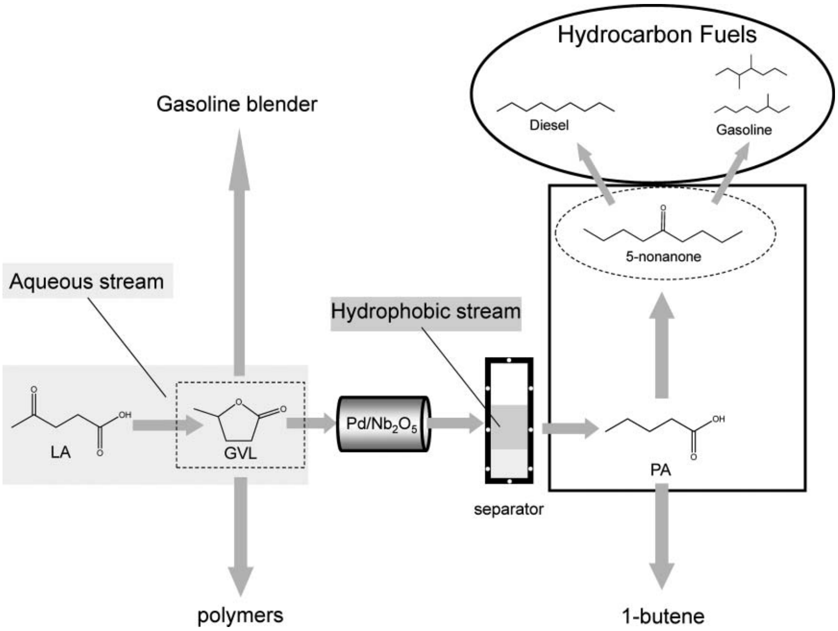

Fig. 2 Applications for the catalytic upgrading of levulinic acid to fuels and chemicals.

The formation of pentanoic acid achieves reduction of the oxygen content of levulinic acid, leading to a less-reactive, hydrophobic intermediate that is appropriate for new upgrading strategies to control reactivity (Table 1, entries 6–8). For example, pentanoic acid can be converted to 5-nonanone by means of ketonization reactions[22] with the release of stoichiometric amounts of CO_2 and water (Fig. 1). We found that, by increasing temperature and decreasing space velocity, this transformation can be carried out over the same Pd/Nb_2O_5 catalyst used to produce pentanoic acid, allowing the direct production of an organic stream enriched in 5-nonanone from aqueous GVL in a single catalytic bed (Table 1, entry 6). The C_9 ketone was produced with an optimized carbon yield of almost 60%, with unreacted pentanoic acid, C_{4-5} alkanes and lower ketones (produced by scission of 5-nonanone) accounting for the rest of the carbon stored in the effluent organic layer that spontaneously separates from water. Although this strategy is beneficial in that it minimizes the number of reactors involved (leading to reduction of capital and operating costs for the process), the number of reactions taking place in a single reactor is high, and control over the individual steps (from GVL to PA to 5-nonanone) is difficult, thus limiting the ultimate yield to the C_9 ketone. This limitation can be overcome by utilizing an additional bed of ceria–zirconia in a cascade approach.[5,16] In this case, the reaction conditions in the first Pd/Nb_2O_5 reactor are adjusted to maximize the yield of pentanoic acid (Table 1, entry 5), which is then converted downstream to 5-nonanone over ceria-zirconia at higher temperatures (Table 1, entry 8). We note that the reaction conditions for the second bed were previously identified using pure pentanoic as feed to maximize the yield to 5-nonanone (Table 1, entry 7). The use of an additional reactor in this dual bed approach is justified by the improved yield to 5-nonanone (84%), which is again obtained in a spontaneously-separating, high purity organic stream.

Fig. 2 outlines several important applications that can be derived from the catalytic strategy described in this communication. For example, the route to upgrade aqueous solutions of levulinic acid to fuels and chemicals involves the formation of intermediate GVL, which has been proposed to be an important precursor for the polymer industry[12] and to be a potential gasoline blending agent.[18] Alternatively, GVL can be converted in a single reactor to pentanoic acid, a hydrophobic product that spontaneously separates from water, whose esters find applications in the perfume and food industries.[23] Additionally, pentanoic acid can be converted, by means of decarboxylation reactions, to 1-butene,[24] a valuable chemical for the production of plastics. We have also shown that pentanoic acid can be upgraded with high yields to 5-nonanone, which has applications as an industrial solvent in paints and resins.[25] The organic stream of 5-nonanone can also serve as a precursor for hydrocarbon fuels of different classes (diesel and gasoline). In particular, 5-nonanone can be converted, by means of hydrogenation/dehydration cycles over bifunctional Pt/Nb_2O_5,[26] to linear nonane, with good cetane number and lubricity to be used as a diesel fuel blender. Additionally, branched C_9 hydrocarbons for use as gasoline components could be obtained by dehydration/isomerization of 5-nonanol (hydrogenation product of 5-nonanone) over a zeolite such as USY.

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