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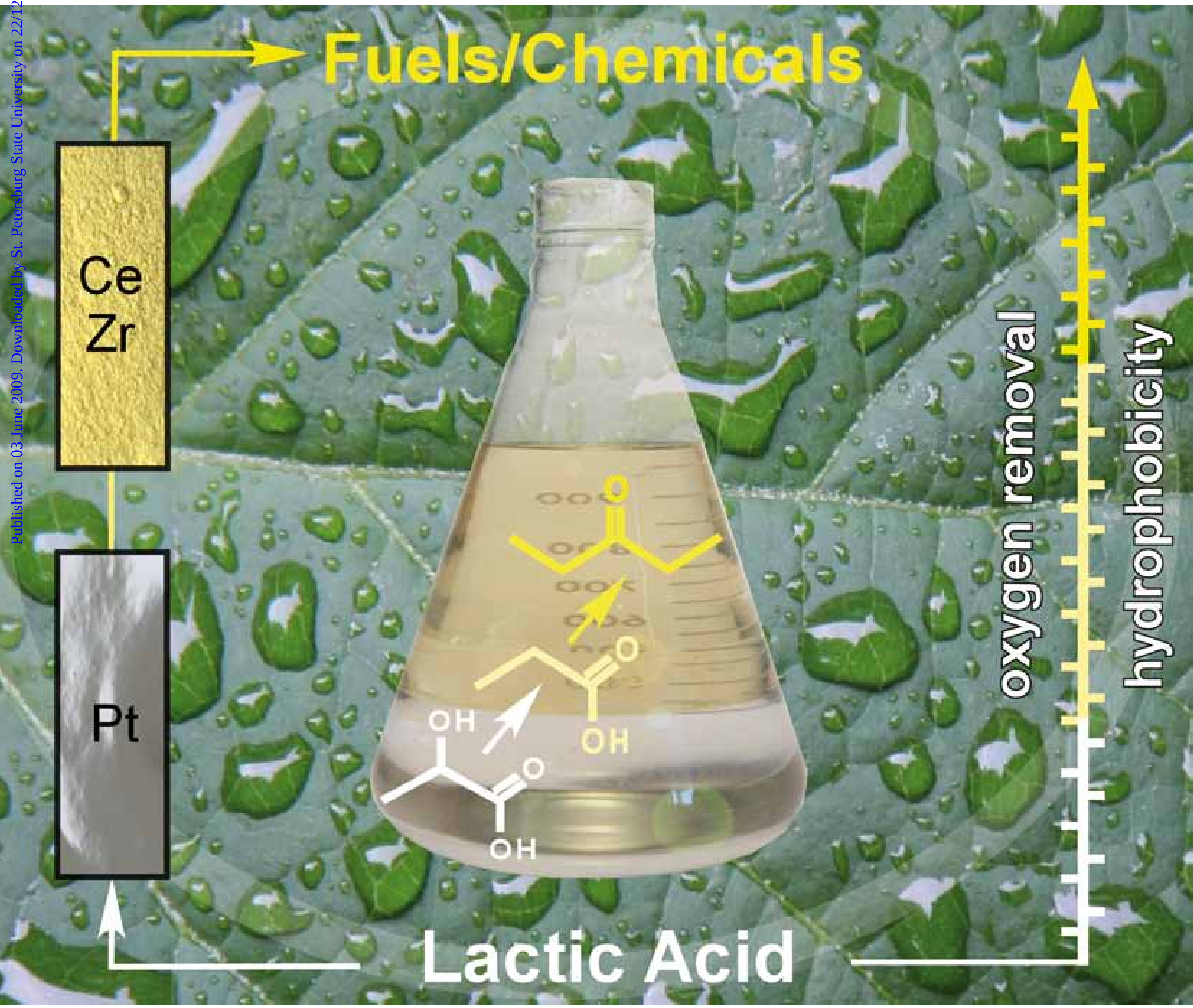

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Catalytic upgrading of lactic acid to fuels and chemicals by dehydration/hydrogenation and C–C coupling reactions†

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Aqueous solutions of lactic acid can be catalytically processed over Pt(0.1%)/Nb_2O_5 into a spontaneously-separating organic layer that can serve as source of valuable chemicals (propanoic acid and C_4–C_7 ketones) and/or can be used to produce high energy-density liquid fuels (C_4–C_7 alcohols). The niobia support plays a key role in the synthesis by catalyzing dehydration and C–C coupling reactions.

Utilization of renewable feedstocks for the chemical industry is becoming ever more important in view of decreasing fossil resources and increased pressure on our environment. In this respect, biomass is a promising candidate to serve as a sustainable source of organic carbon for the production of industrial chemicals.[1] However, establishment of a renewable chemical industry, that is cost-competitive with the current one based on petroleum, requires development of new processes to convert biomass-derived feedstocks into valuable products. Unlike petroleum feedstocks which possess low extents of functionality, the compounds in biomass-derived resources contain an excess of oxygenated groups, leading to high and uncontrolled reactivity. Consequently, the challenge in the emerging renewable chemical industry is to develop methods to decrease the oxygen content of these molecules and, with it, to direct the conversion to the desired final products.[2]

Lactic acid (2-hydroxypropanoic acid), containing adjacent hydroxyl and carboxylic groups, can be considered to be a model of an over-functionalized biomass-derived molecule. It can be obtained from biomass with low cost by bacterial fermentation, and it has a growing market because of its multiple applications.[3] In addition, lactic acid has been suggested to be one of the most promising building blocks for the future growth of a renewable chemical industry.[4] Previous works have reported the direct conversion of lactic acid to products such as acetaldehyde,[5] acrylic acid[5,6] and propanoic acid.[7] Herein we propose a new strategy to upgrade this resource into valuable chemicals. The general approach consists of a partial reduction of the oxygen content of the molecule leading to less reactive intermediates that still contain sufficient functionality for further upgrading to valuable chemicals. One advantage of this approach is that we can accomplish both the removal of oxygen and the upgrading of intermediates in a single reactor and under high water environments by using a water-stable bifunctional Pt/Nb_2O_5 catalyst.

Fig. 1 shows the reaction pathways that we have employed to upgrade lactic acid into valuable chemicals over Pt/Nb_2O_5. The reaction scheme is based on the formation of two less-oxygenated reaction intermediates: propanoic acid and acetaldehyde (each labeled with a square in Fig. 1). The formation of propanoic acid from lactic acid involves the removal of the hydroxyl group through C–O cleavage, which can be achieved by direct C–O hydrogenolysis (on platinum sites) or can take place over the bifunctional Pt/Nb_2O_5 catalyst through dehydration (on the acidic support) followed by hydrogenation (on metal sites). The formation of acetaldehyde involves C–C bond cleavage through decarbonylation/decarboxylation reactions, catalyzed by platinum sites and also through acid-catalyzed decarbonylation.[8] After the two intermediates have been formed, the presence of niobia can selectively guide the synthesis (by C–C coupling reactions) towards more valuable products instead of allowing these intermediates to undergo further reduction reactions (*e.g.*, leading first to propanol and ethanol and subsequently to propane and ethane). Thus, propionic acid can be converted into pentanones by ketonization, and acetaldehyde can be upgraded into C_4-carbonyls (mainly 2-butanone) by aldol-condensation reactions. These compounds can be upgraded to larger ketones (in the C_6 and C_7 range) by means of successive aldol condensation reactions with the previously formed acetaldehyde, which should be present in the reactor in significant concentrations because the acidity of niobia favors decarbonylation of lactic acid.[8] In this respect, catalysts consisting of low metal loadings supported on niobia have been previously reported to be materials for condensation of ketones, such as acetone, to larger carbonyls such as methyl isobutyl ketone.[9] Additionally, niobia was chosen as a support because it provides excellent stability as well as sufficiently strong acidity to carry out dehydration reactions of alcohols under water environments.[10]

Table 1 summarizes experimental results (carbon distribution and carbon selectivities) for the conversion of a 60 wt% aqueous lactic acid solution (employing a hydrogen co-feed at 80 cm^3(STP) min^{-1}) at 623 K and 57 bar and at various space velocities over bifunctional Pt(0.1%)/Nb_2O_5. These results were compared with those obtained for a pure monofunctional hydrogenation catalyst, Pt(0.1%)/Vulcan, to study the important role of niobia in the process. Vulcan was selected

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Table 1 Carbon distribution and carbon selectivities for lactic acid conversion at 623 K and 57 bar over Pt(0.1%)/Vulcan and Pt(0.1%)/Nb_2O_5. Values in parentheses refer to methane. CO_x indicates CO and CO_2. The balance in carbon selectivities is closed to 100% by inclusion of other products such as cycloketones and lactones. The high degree of reproducibility of these data and the high stability of the catalyst with respect to time-on-stream are documented in the ESI.† Carbon balances range from 88 to 110%

Catalysts	Pt/Vulcan			Pt/Nb_2O_5		
WHSV (h^{-1})	0.8	1.7	5.0	0.8	1.7	5.0
Carbon gas-phase effluent (%)	75	70	64	43	42	41
Carbon aqueous-phase effluent (%)	25	30	36	10	12	14
Carbon organic-phase effluent (%)	—	—	—	47	46	45
Total carbon selectivity (%)						
CO_x	54	47	40	26	26	37
Propanoic acid + esters	9	7	5	19	25	18
Acetaldehyde	1	7	16	0	2	9
Ethanol	18	12	6	4	4	4
C_4–C_7 Condensation products	1	1	0	24	18	19
C_1-C_7 Alkanes (methane)	15 (10)	9 (8)	4 (3)	22 (2)	17 (2)	4 (1)
Propanol/acetone	1	0	0	4	4	2
Lactic acid	0	13	25	0	0	0

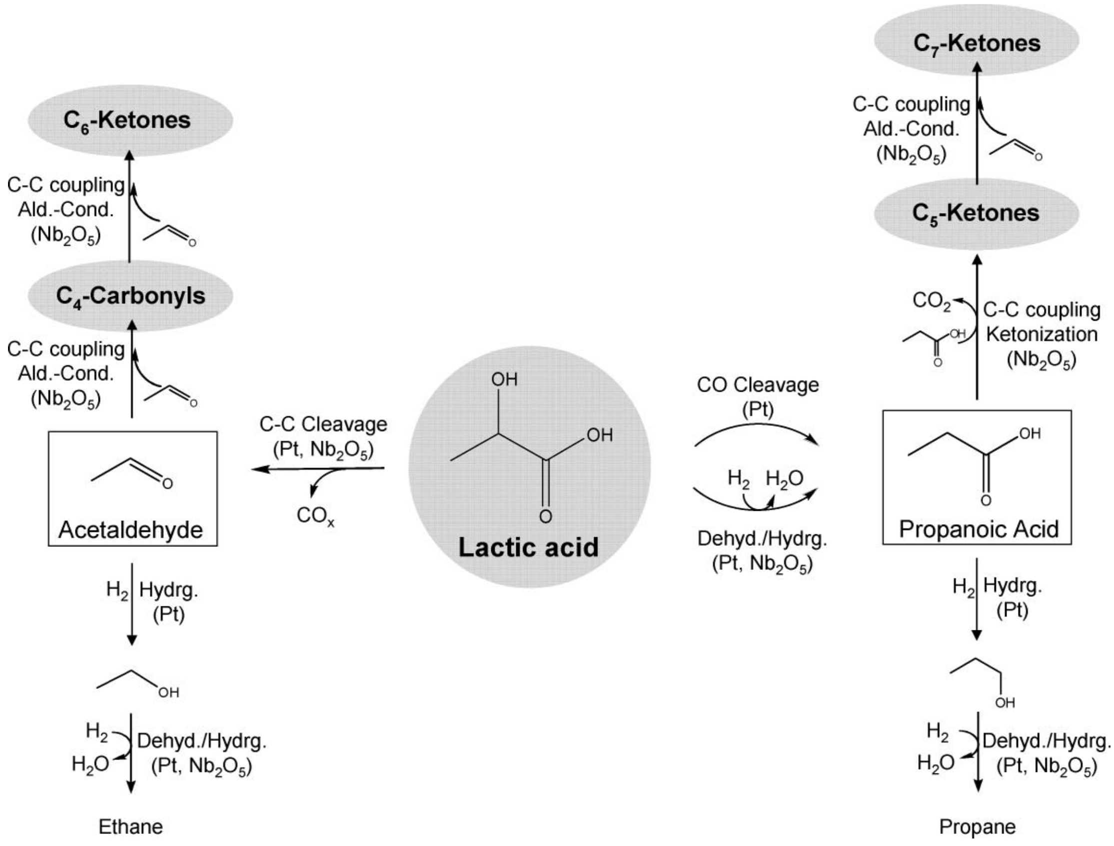

Fig. 1 Reaction pathways for lactic acid dehydration/hydrogenation and C–C coupling over Pt/Nb_2O_5.

as a support because of its chemical inertness derived from its low level of functionality. Pt(0.1%)/Vulcan showed lower activity than Pt(0.1%)/Nb_2O_5 at the same conditions (lactic acid conversion of 76% *versus* 100% at weight hourly space velocity, WHSV = 5.0 h^{-1}), indicating a promotional effect of niobia for the overall process. In terms of carbon distribution, Pt(0.1%)/Vulcan produced a higher amount of product carbon in the gas phase (75% of reacted carbon at 0.8 h^{-1} and 100% conversion) while in the case of the bifunctional Pt(0.1%)/Nb_2O_5 catalyst, about 60% of the reacted carbon remained in the liquid phase for all conditions studied. Importantly, unlike Pt(0.1%)/Vulcan, lactic acid conversion over Pt(0.1%)/Nb_2O_5 produced the onset of an organic phase that spontaneously separated from water and accounted for almost the 50% of the total reacted carbon at 100% conversion. This behaviour is a clear indication that different reaction pathways are operative depending on the nature of the catalyst used. Thus, lactic acid reacted on Pt(0.1%)/Vulcan at high flow rates (WHSV = 5.0 h^{-1}) to produce mostly CO and CO_2 (40% carbon) and acetaldehyde–ethanol (22%), with lower amounts of methane (3% of the carbon, included in C_1–C_7 alkane in Table 1) and propanoic acid (5%). Remarkably, no C_4–C_7 condensation products were detected at these conditions, while 25% of the carbon remained unreacted as lactic acid. When lower space velocities were used (WHSV = 0.8 h^{-1}), lactic acid conversion was complete, but CO and CO_2 accounted for most of the detected carbon (54%), while acetaldehyde (1%) was almost completely hydrogenated to ethanol (18%). Interestingly, the amount of propanoic acid (and its ethyl-ester) increased at the low space velocity (9%, with only 1% C_4–C_7 condensation products) as well as methane, which accounted for 10% of the detected carbon. In view of these results, it can be concluded that, at these conditions, Pt(0.1%)/Vulcan favoured C–C cleavage reactions leading to C_1 species (CO, CO_2 and CH_4) and C_2 species to a lower extent (acetaldehyde–ethanol), whereas this catalyst was not effective for C–O cleavage reactions leading to C_3 species such as propanoic acid. In agreement with this behaviour, it has been reported that metals such as Pt are active and selective for cleavage of C–C bonds (*versus* C–O cleavage) in oxygenated hydrocarbons.[11] Importantly, C–C condensation reactions were not significant on the monofunctional Pt(0.1%)/Vulcan, since negligible amounts of C_4–C_7 ketones were observed.

Lactic acid reacted completely over the bifunctional Pt(0.1%)/Nb_2O_5 catalyst at high space velocities (WHSV = 5.0 h^{-1}) to produce mainly CO and CO_2 (37% carbon), acetaldehyde–ethanol (13%), and, importantly, a significant amount of propanoic acid (18%) and C–C condensation products (19%). A decrease in the space velocity to 0.8 h^{-1} caused a slight increase in the amount of C–C condensation products (24%) at the expense of acetaldehyde that, as pointed out in Fig. 1, preferentially formed C_4-carbonyls *versus* direct hydrogenation to ethanol (stable at 4%, Table 1). It is noteworthy that almost all of the condensation products spontaneously separated from water to form an organic phase, and only negligible amounts of these compounds remained in the aqueous phase. The low space velocities also favored the formation of C_1–C_7 alkanes but, unlike Pt(0.1%)/Vulcan, significant amounts of methane were not detected with the niobia-supported catalyst (2%). The key role of the niobia support is clearly observed by analyzing the main differences between both catalysts. In particular, Pt(0.1%)/Nb_2O_5 achieves C–C coupling reactions, such as ketonization and aldol condensation, leading to C_4–C_7 condensation products stored in the organic layer, whereas Pt(0.1%)/Vulcan catalyzed mainly C–C cleavage reactions leading to C_1 species (CO_x and methane accounting for almost 65% of the reacted carbon at low space velocities) with the corresponding loss of carbon to the gas phase. Additionally, the higher amount of propanoic acid produced by Pt(0.1%)/Nb_2O_5 (19% of the carbon at WHSV = 0.8 h^{-1}) in comparison with Pt(0.1%)/Vulcan (9%) supports the hypothesis that the higher reactivity of platinum on an acidic support such as niobia is caused by a two-step dehydration–hydrogenation process to achieve C–O cleavage instead of C–C breaking.[11] Finally, we note here that both catalysts were prepared using the same low loading of Pt (0.1%) to minimize catalyst costs for our process. While it would be interesting to study the catalytic effect of varying the dispersion of the Pt nanoparticles, we do not expect this effect to be large. In particular, hydrogenation processes (as involved in the bi-functional catalysis described here) are typically structure insensitive,[12] and we have observed elsewhere that the selectivity for C–C *versus* C–O bond cleavage reactions does not change significantly with Pt particle size for catalytic processing of oxygenated hydrocarbons.[13]

The results detailed above indicate that a low metal content bifunctional Pt(0.1%)/Nb_2O_5 catalyst can efficiently process aqueous solutions of lactic acid into a spontaneously-separating organic layer that has several uses. On one hand, this organic effluent can be employed as source of valuable chemicals. The composition of the organic phase (specifically the liquid obtained after lactic acid processing at WHSV = 1.7 h^{-1}, Table 1) is shown in Fig. 2, A1, and included propanoic acid and esters (46% of the carbon of this phase) and C_4–C_7 ketones (35%) in important amounts, with C_4–C_7 alkanes, acetone and alcohols accounting for the rest of the carbon. Taking advantage of the different boiling points of propanoic acid[14] (413 K) and the C_4–C_7 ketones[15] (C_4: 353 K, C_5: 373 K, C_6: 398 K and C_7: 427 K), the oil could be separated by fractional distillation into its valuable components: propanoic acid serving as a preservative for foods and feeds,[14] whereas the ketones have widespread use as solvents and chemical intermediates.[15]

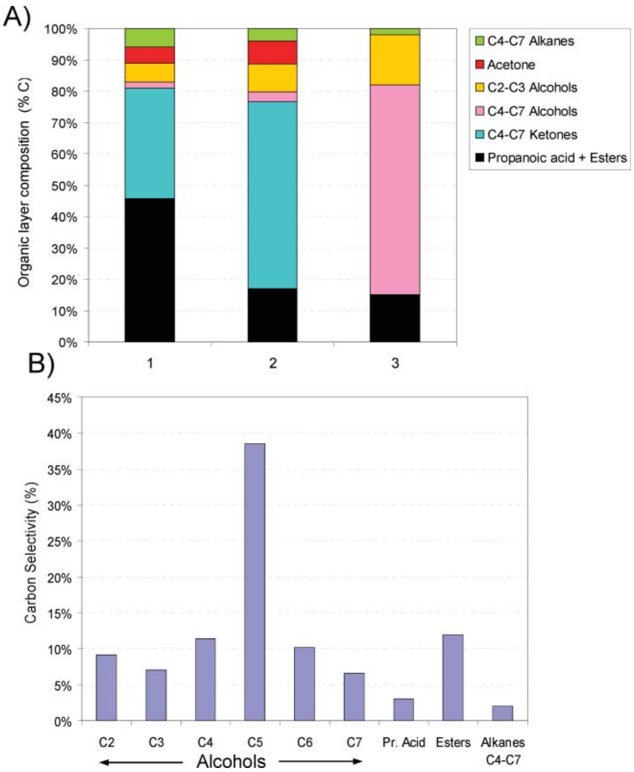

Fig. 2 A) Composition of the organic layer obtained for the conversion of a 60 wt% solution of lactic acid in water over 1: Pt(0.1%)/Nb_2O_5 at 623 K, 57 bar and WHSV = 1.7 h^{-1}; 2: Pt(0.1%)/Nb_2O_5 + $Ce_{0.5}Zr_{0.5}O_2$ double bed at 623 K, 57 bar and WHSV = 1.7 h^{-1} (based on first bed); 3: organic layer obtained from 2 after hydrogenation over Ru(5%)/C at 373 K, 35 bar and WHSV = 1.3 h^{-1} (H_2 co-feed at 50 cm^3(STP)/min). B) Composition of organic effluent obtained from 3; C_2–C_7 represent the number of carbons of the corresponding alcohols.

On the other hand, the spontaneously-separated organic phase could be upgraded (without the need of separation) to high energy-density liquid-fuels (composed of C_4–C_7 alcohols) in a cascade-mode approach. In this approach, the remaining propionic acid and esters can first be converted into pentanones *via* ketonization by adding a ceria-zirconia bed[2] and using the same conditions of pressure and temperature, as shown in Fig. 2, A2. The organic effluent obtained with the Pt(0.1%)/Nb_2O_5 + $Ce_{0.5}Zr_{0.5}O_2$ double-bed arrangement contained approximately 55% of the feed carbon (*versus* 46% for the Pt(0.1%)/Nb_2O_5 single bed configuration, Table 1), and this organic liquid was enriched in C_4–C_7 ketones (60% of the carbon, pentanone being the main compound), with acetone (7%) and C_2–C_3 alcohols (16%) also being present in the oil in significant amounts. Remarkably, the double-bed reactor showed good stability for the conversion of propanoic acid and its esters to pentanone for more than 2 days on stream, and the fraction of these compounds that remained unreacted (17%, Fig. 2, A2) could be totally converted by using lower space velocities in the double-bed configuration. Finally, this organic effluent enriched in C_4–C_7 ketones can be quantitatively converted into the corresponding alcohols (only 0.5% the carbon was lost in the gas phase) with a Ru/C catalyst at low temperatures (Fig. 2, A3). As a result, the final processed liquid contained a mixture of alcohols in the range of C_4–C_7 that could be suitable for use as high energy-density fuel. We note that the reduction process with Ru/C at 373 K also caused a partial hydrogenation of propanoic acid to 1-propanol whereas the esters remained unreacted. In terms of the alcohol distribution, pentanol was the most abundant alcohol and ethanol, 1-propanol and 2-propanol (from the hydrogenation of the acetone) were also present in the liquid in significant amounts (Fig. 2, B).

In summary, we report a catalytic route to selectively guide the conversion of lactic acid (an important low-cost biomass-derived commodity chemical with an expected growing market) toward valuable products (propanoic acid and C_4–C_7 ketones) using a low metal-content Pt(0.1%)/Nb_2O_5 catalyst. A novel aspect of the approach outlined here is that by using a bifunctional catalyst containing metal and acid sites, the series of required reactions leading to the desired products (*e.g.*, dehydration–hydrogenation and C–C coupling) can be carried out in a single flow reactor, thus reducing capital and operating costs for the process. The niobia support plays a crucial role in directing the synthesis to valuable compounds by catalyzing C–C coupling reactions such as aldol-condensation and ketonization, instead of C–C cleavage reactions that take place over monofunctional Pt/Vulcan and lead to loss of carbon in the gas phase. This conversion of lactic acid over Pt(0.1%)/Nb_2O_5 maintains approximately 50% of the feed carbon in an organic effluent phase (rich in valuable products) that spontaneously separates from the aqueous layer, thus eliminating the need to remove these products from water. This oil could be used as a direct source of valuable chemicals and/or can be potentially upgraded to liquid fuels. Finally, the approach outlined here of oxygen removal and subsequent upgrading of intermediates in a single reactor is flexible in that it could be applied not only to lactic acid but also to other over-functionalized biomass-derived molecules. One especially interesting example would be the catalytic processing of levulinic acid, which can be derived from waste biomass sources (*e.g.*, paper mill sludge, urban waste paper, agricultural residues) by the Biofine process.[16]

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