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Quantitative formation of gamma-valerolactone from furfural aldehyde with a recyclable acidic system and Ru-MACHO catalyst under a H_2 atmosphere

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This study presents an efficient catalytic system for the direct conversion of carbohydrate-derived furfural aldehyde (FA) into γ-valerolactone (GVL) in high yields. Using a homogeneous Ru-MACHO-BH catalyst in combination with a recyclable solid acid as co-catalyst, GVL is obtained in up to 99% NMR yield under the optimized conditions of 0.5 mol% Ru-MACHO-BH, 5 mol% Amberlyst-36, ethanol, 30 bar H_2, 120 °C, and 24 h. Full conversion and complete selectivity toward GVL are achieved with 0.5 mol% Ru-MACHO-BH and 5 mol% Amberlyst-36. The solid acid co-catalyst can be reused for at least ten cycles provided that Amberlyst-36 is regenerated with H_2SO_4(aq) between runs, as the resin otherwise shows significant deactivation after three cycles. The robustness of the method was evaluated through scale-up experiments up to 20 mmol (1.9 g) of FA. At this scale, conversions decrease to 65–72% when using 0.5 mol% Ru-MACHO-BH, maintaining 100% selectivity to GVL, whereas increasing the catalyst loading to 1 mol% restored full conversion and quantitative GVL formation. Overall, this work demonstrates a selective and scalable approach to FA valorization under well-defined reaction conditions.

Broader context

Developing direct and recyclable pathways for converting raw biomass into targeted end-products is essential for establishing viable and sustainable valorised biogenic resources. Equally critical is the ability to carry out these transformations in high yields under the mildest and least waste-generating conditions possible. Gamma-valerolactone (GVL) is biodegradable and a promising biomass valorisation compound due to its potential applications as *e.g.* a biofuel, industrial chemical, and solvent. On the other end, furfural is an established industrial platform chemical arising from hemicellulosic material. Consequently, developing an environmentally benign synthetic route to GVL from furfural would provide access to a fuel and chemical intermediate that is both high-value and genuinely sustainable. However, to the best of our knowledge, a system remains elusive that affords both a direct, recyclable, and high-yielding method for GVL production from furfural that is at the same time operating under mild conditions. Our protocol is first-in-class to show the proof-of-concept of direct transformation of furfural to GVL in quantitative yields under mild conditions using a hybrid combination of homogeneous and heterogenous catalysis. Additionally, the acid that is fully recyclable over at least ten cycles, demonstrating a substantial improvement over state-of-the-art. Moreover, we employ waste-free H_2 as H-donor, a great advance over sacrificial organic H-donors.

Introduction

The valorization of biomass derived waste streams into useful chemical products is central to advancing a circular and sustainable chemical economy.[1] Although numerous catalytic strategies have been developed for the upgrading of biogenic substrates, many still rely on corrosive mineral acids, stoichiometric additives, or conditions that generate significant waste. These limitations reduce process sustainability and viability and hinder industrial implementation. Consequently, there is a strong incentive to design catalytic systems that combine high efficiency with recyclability and minimal environmental burden. Furfural (FAL), obtained from the dehydration of xylose and ultimately from hemicellulose, is one of the most established platform molecules in biorefinery schemes.[2] Its transformation into γ valerolactone (GVL)[3] is particularly attractive, as GVL serves as a versatile solvent, fuel additive, and intermediate for polymer and fine chemical synthesis. Direct conversion of furfural to GVL under reductive and acidic conditions offers a streamlined route that avoids multistep processing.[4] Furfural, readily accessible from hemicellulose-derived xylose, is an attractive and complementary platform molecule for γ-valerolactone (GVL) production within integrated biorefinery schemes.[5] γ-Valerolactone (GVL) is widely

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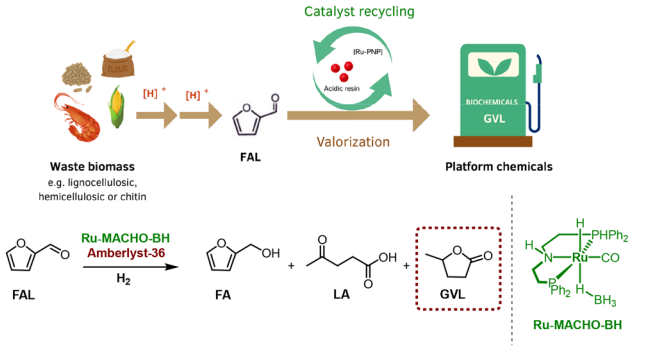
regarded as one of the most promising sustainable and well-defined platform molecules accessible from biomass.[6] It can be produced from biogenic carbohydrates *via* a sequence of catalytic transformations involving *e.g.* lignocellulosic intermediates. Owing to its high stability, low toxicity, and favourable physicochemical properties, GVL has attracted significant interest as a biofuel or fuel additive, a renewable and environmentally benign solvent, and a versatile intermediate for the synthesis of value-added chemicals, including polymers and pharmaceutical precursors.[7] Conventional GVL syntheses predominantly proceed from cellulose *via* levulinic acid,[8] which is expensive to isolate. In contrast, the direct conversion of furfural to GVL under combined reductive and acidic conditions allows access to GVL without isolation of expensive intermediates, thereby reducing overall process complexity and cost.[4a] Compared to pathways based on 5-hydroxymethylfurfural, which typically involve additional oxidative or rehydration transformations prior to hydrogenation,[9] the furfural-based route offers a more concise strategy that directly exploits the structural features of hemicellulose-derived feedstocks.

We recently demonstrated that the combination of aqueous H_3PO_4, Ru-MACHO-BH, and H_2 enables this single-operation transformation.[4b] However, the use of bulk mineral acid introduces challenges related to waste generation, separation, and catalyst compatibility. Solid acid catalysts provide a promising alternative, as they deliver strong Brønsted acidity while enabling straightforward separation and reuse. Sulfonated polystyrene–divinylbenzene resins such as Amberlyst-36 have been widely applied in biomass upgrading, dehydration, esterification, and related transformations due to their high acid site density, hydrothermal robustness, and compatibility with liquid phase processing.[10] Their heterogeneous nature allows the catalyst to be recovered by simple filtration, and the sulfonic acid groups are generally resistant to leaching under aqueous or biphasic conditions. Importantly, these resins can be regenerated through washing protocols that remove adsorbed organic species, while mild thermal or solvent treatments restore full activity.[11] As a result, acidic resins often maintain catalytic performance over many cycles, aligning well with the principles of green chemistry.[12]

In this work, we show that replacing the vastly supra-stoichiometric H_3PO_4(aq) medium with catalytic quantities of Amberlyst-36 not only dramatically reduces the acid-loading requirement but also enhances overall process sustainability. The resin assisted system affords GVL in quantitative yield, and the solid acid can be recovered and reused for at least ten consecutive cycles without any detectable loss in activity. This approach demonstrates that recyclable solid acids can effectively replace mineral acids in reductive catalytic upgrading of furfural, offering a more sustainable pathway toward the production of bio derived GVL (Scheme 1).

Results and discussion

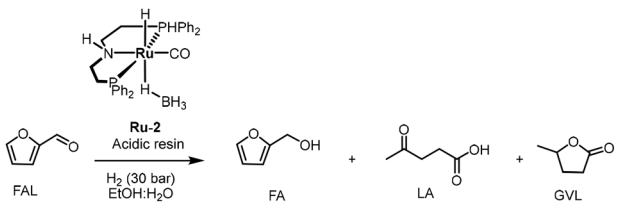
Screening of acidic resins and reaction conditions was carried out using Ru-MACHO-BH (**Ru-2**) as the hydrogenation catalyst under 30 bar H_2. The starting conditions were selected based



Scheme 1 Schematic representation of the approach followed in this work.

on our previous work on the same system, where the transformation was conducted using a stoichiometric amount of acid.[4b] As shown in entry 1 in Table 1, 2 mol% **Ru-2** and 5 mol% Amberlyst-36 provided 45% yield of GVL in 3 : 7 EtOH : H_2O at 120 °C for 24 hours. The reported distributions of furfural (FA), levulinic acid (LA), and γ-valerolactone (GVL) correspond to the final reaction composition measured after 24 h of reaction. Complete conversion was observed, with no detectable formation of furfural (FA) or levulinic acid (LA). Instead, the formation of humins was evidenced by the appearance of a black solid residue in the reaction mixture. As part of the

Table 1 Reaction conditions screening with **Ru-2** as hydrogenation catalyst



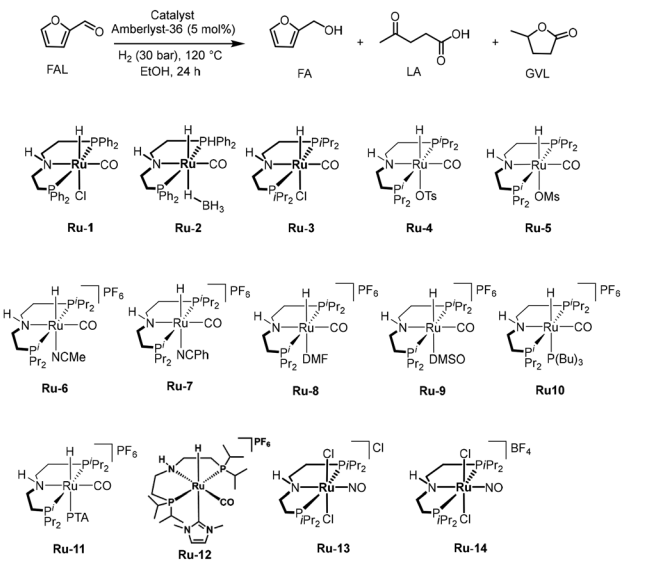
Entry[a]	Acidic resins (mol%)	EtOH : H_2O	Conv.[b] (%)	FA : LA : GVL[b]	S^c (%)
1	Amberlyst-36 (5)	3 : 7	100	0 : 0 : 45	45
2	Amberlyst-36 (2.5)	3 : 7	100	0 : 0 : 36	36
3[d]	Amberlyst-36 (5)	3 : 7	100	0 : 22 : 28	50
4	Amberlyst-36 (5)	0 : 10	100	0 : 0 : 13	13
5	Amberlyst-36 (5)	5 : 5	100	0 : 0 : 60	60
6	Amberlyst-36 (5)	7 : 3	100	0 : 0 : 75	75
7	Amberlyst-36 (5)	9 : 1	100	0 : 0 : 55	55
8	Amberlyst-36 (5)	9.5 : 0.5	100	0 : 0 : 92	92
9	Amberlyst-36 (5)	10 : 0	100	0 : 0 : 100	100
10	Amberlyst-15 (5)	3 : 7	100	0 : 0 : 50	50
11	Amberlyst-15 (5)	10 : 0	100	0 : 0 : 39	39
12	Amberlite IR120 (5)	3 : 7	100	73 : 0 : 0	68
13	Amberlite IR120 (2)	3 : 7	100	54 : 0 : 0	54
14[ef]	Amberlyst-36 (5)	3 : 7	100	0 : 0 : 71	71
15[e]	Amberlyst-36 (5)	10 : 0	100	44 : 0 : 55	99

[a] Standard reaction conditions: 0.79 mmol of FAL (76 mg), 2 mol% of **Ru-2** in a mixture of EtOH:H_2O (2.0 mL), H_2 (30 bar), 24 h at 120 °C. [b] Conversion and yield were both determined by crude ^{1}H-NMR. Dimethyl sulfone was used as internal standard. Reactions are reproducible within an error margin of ±5%. The reaction were reproduced at least three times to corroborate the results. [c] Selectivity towards GVL-route. [d] 1 mol% of **Ru-2**. [e] 80 °C. [f] 72 h.

preliminary screening, we independently lowered the loading of each catalytic component to assess their individual relevance under the selected reaction conditions. Specifically, reducing the amount of Amberlyst-36 from 5 to 2.5 mol% while keeping Ru-MACHO-BH (**Ru-2**) at 2 mol%, or decreasing the **Ru-2** loading from 2 mol% to 1 mol% while maintaining Amberlyst-36 at 5 mol%, both using the same EtOH/H_2O (3 : 7) solvent mixture, resulted in a marked decrease in GVL yield (36% and 28%, respectively; entries 2 and 3). These results clearly indicate that both the acidic resin and the hydrogenation catalyst play a crucial role at the initially chosen loadings, which were therefore selected as benchmark conditions for subsequent studies. We continued our screening, changing the solvent ratio of EtOH and H_2O also had a major impact on GVL-route selectivity and yield. Thus, as shown in entries 4–9, gradually increasing the EtOH content improves the yield from 13% in 0% EtOH (*i.e.*, 100% H_2O) in entry 4 to quantitative in 100% EtOH in entry 9. The increase in GVL yield with higher ethanol content can be attributed to ethanol's dual role as both solvent and hydrogen donor, which facilitates the transfer hydrogenation steps leading to GVL formation. In contrast, water-rich media favour competing side reactions, such as rehydration and humins formation, resulting in lower selectivity. Moreover, ethanol improves the solubility and stabilization of organic intermediates and can enhance catalyst efficiency. Collectively, these effects shift the reaction network toward selective GVL formation as the EtOH/H_2O ratio increases. Replacing Amberlyst-36 other solid acids led to inferior outcomes. Thus, Amberlyst-15 was slightly better than Amberlyst-36 in 3 : 7 EtOH : H_2O with 50% yield (entry 10), but in 100% EtOH merely 39% GVL was obtained (entry 11). Likewise, the selectivities were equally low. Worse yields but better selectivities were observed with Amberlite IR120. Thus 5 mol% Amberlite IR120 afforded no GVL but 68% FA, and similarly 2 mol% provided 54% FA. The different catalytic behaviours observed for the different resins can be ascribed to their distinct physicochemical properties. Amberlyst-36 exhibits a higher sulfonic acid site density and overall acid capacity than Amberlyst-15, resulting in stronger Brønsted acidity and a greater number of accessible active sites. These features enhance the rate of the acid-catalysed steps involved in the GVL route, leading to improved activity and selectivity. Furthermore, differences in resin morphology and porosity may influence mass-transfer characteristics and reactant accessibility, further contributing to the observed performance differences. By comparison, Amberlite IR-120, despite being a strongly acidic sulfonated resin, displays a lower acid site accessibility and less favourable structural properties than Amberlyst-36, which can limit its catalytic efficiency under the same conditions. Finally, lowering the reaction temperature to 80 °C proved detrimental to GVL production albeit the selectivity seemed to increase. Thus, in 3 : 7 EtOH : H_2O a 71% yield of GVL could be obtained after 72 hours (entry 14) with full conversion, representing an improvement over the 45% achieved at 120 °C, and in pure EtOH a large amount of FA (44%) was still present after 24 hours leading to merely 55% yield of GVL albeit at 99% selectivity for the GVL-route.

We then evaluated a series of additional hydrogenation catalysts under identical conditions (EtOH, 120 °C, 24 h) to benchmark their performance against the reference system (Table 2). A rather large library of Ru-PNP type catalysts were tested, many of which were recently developed in our own lab.[13] Commencing with **Ru-1**, 13% LA and 85% GVL were obtained (98% selectivity, entry 1), which was slightly inferior to **Ru-2** (100% yield, entry 2). This difference can probably be explained by the higher tendency of **Ru-2** than **Ru-1** to be thermally activated in the absence of a base. Gratifyingly, **Ru-2** could be

Table 2 Catalyst and catalytic loading screening for furfural hydrogenation reaction in acidic conditions



Entry[a]	Catalyst (mol%)	Conv.[b] (%)	FA : LA : GVL[b]	GVL-route selectivity (%)
1	**Ru-1** (2 mol%)	100	0 : 13 : 85	98
2	**Ru-2** (2 mol%)	100	0 : 0 : 100	100
3	**Ru-2** (1 mol%)	100	0 : 0 : 100	100
4	**Ru-2** (0.5 mol%)	100	0 : 0 : 100	100
5[c]	**Ru-2** (0.5 mol%)	100	21 : 41 : 37	99
6	**Ru-2** (0.5 mol%)	100	0 : 23 : 88	100
7[d]	**Ru-2** (0.25 mol%)	100	0 : 25 : 75	100
8	**Ru-2** (0.1 mol%)	86	0 : 75 : 9	84
9	**Ru-3** (2 mol%)	100	0 : 81 : 18	99
10	**Ru-4** (2 mol%)	100	0 : 0 : 61	61
11	**Ru-5** (2 mol%)	100	0 : 28 : 44	72
12	**Ru-6** (2 mol%)	100	0 : 10 : 89	99
13	**Ru-7** (2 mol%)	100	17 : 13 : 55	85
14	**Ru-8** (2 mol%)	100	0 : 60 : 40	100
15	**Ru-9** (2 mol%)	100	0 : 50 : 55	100
16	**Ru-10** (2 mol%)	100	0 : 0 : 100	100
17	**Ru-10** (0.5 mol%)	100	0 : 63 : 40	100
18	**Ru-11** (2 mol%)	100	20 : 47 : 20	87
19	**Ru-12** (2 mol%)	100	0 : 50 : 13	63
20	**Ru-13** (2 mol%)	100	0 : 55 : 0	55
21	**Ru-14** (2 mol%)	100	0 : 64 : 0	64

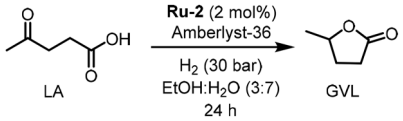
[a] Standard reaction conditions: 0.79 mmol of FAL (76 mg), 2 mol% of **Ru-2** in a mixture of EtOH : H_2O (2.0 mL), H_2 (30 bar), 24 h at 120 °C. PTA = (1,3,5-triaza-7-phosphaadamantane). [b] Conversion and yield were both determined by crude ^{1}H-NMR. Dimethyl sulfone was used as internal standard. Reactions are reproducible within an error margin of ±5%. The reactions were reproduced to corroborate the results. [c] 100 °C. [d] 18 hours.

lowered in catalyst loading while maintaining an excellent yield of GVL. Thus, with either 1 mol% or 0.5 mol%, **Ru-2** quantitative yields of GVL are obtained (entries 3 and 4). When lowering the temperature to 100 °C, the selectivity remained excellent, but the GVL yield dropped to 37% (entry 5) suggestion that the reaction is incomplete after 24 hours. We did not test extending the reaction time. Shortening the reaction time to 18 hours at 120 °C led to a slightly lower yield of 88% (entry 6). Further dropping the catalyst loading of **Ru-2** to 0.25 mol% led to 73% yield but still with 100% selectivity towards GVL (entry 7), where with 0.1 mol% both yield (8%) and selectivity (70%) drop (entry 8). Changing the *P*-substituents from phenyls in **Ru-1** and **Ru-2** to isopropyls in **Ru-3** had a vast detrimental effect on GVL yield (18%) but kept selectivity at 99% (entry 8). Comparing the result with the *P*-phenyl congener **Ru-1**, there appears to be a significant detrimental effect on LA hydrogenation in the *P*-isopropyl based catalyst. Interestingly, exchanging the chlorido with the sulfonato ligands OTs (tosylsulfonato) in **Ru-4** or OMs (methanesulfonato) in **Ru-5** both resulted in significantly improved GVL yields. Thus, **Ru-4** led to 61% GVL (61% selectivity, entry 9), and **Ru-5** gave 44% GVL (72% selectivity, entry 10). We then tested complex salt derivatives of **Ru-3** as characterization of the *P*-isopropyl complex salts are significantly more straightforward than of the *P*-phenyl congeners. Thus, **Ru-6** to **Ru-12** are all complex salts with the chlorido unit replaced by an L-type ligand and with $PF6^-$ as counter anion. With **Ru-6** (MeCN as L-type ligand), a dramatic improvement was observed compared to the parent **Ru-3**, with similar excellent selectivity (99%) but with 89% GVL and 10% LA (entry 12). Exchanging MeCN with the weaker coordinating ligand PhCN in **Ru-7** surprisingly led to an inferior result with both a lower selectivity (85%), 17% FA, 13% LA, and 55% GVL (entry 13). The selectivity was restored to excellent in **Ru-8** (DMF as L-type ligand), but only 40% GVL was obtained, the remainder being LA (entry 14). In the solvato complex salt **Ru-9** (DMSO as L-type ligand), selectivity remains excellent and the GVL yield improves slightly to 55%, the remainder again being LA (entry 15). When changing to phosphine derivatives in **Ru-10** and **Ru-11**, using $PtBu_3$ (**Ru-10**) resulted in a remarkable excellent result of quantitative amount of GVL, potentially challenging **Ru-2** as the best catalyst (entry 16). However, upon lowering the catalyst loading of **Ru-10** to 0.5 mol%, merely 40% GVL was obtained (100% selectivity, entry 17). With PTA (1,3,5-triaza-7-phosphaadamantane, **Ru-11**), a relatively low selectivity if 87% and merely 20% GVL were observed (entry 18). Employing the NHC-type (N-heterocyclic carbene) ligand IMe (1,3-dimethylimidazole-2-ylidene) in **Ru-12** led to both poor selectivity (63%) and low overall GVL yield (13%, entry 19). Finally, we turned to investigating the NO congener of **Ru-3** where the carbonyl is exchanged by a nitrosyl. The Cl^- salt (**Ru-13**) and $BF4^-$ salt (**Ru-14**) both resulted in poor results with no GVL formed and 55% and 64%, respectively, of LA formed (entries 20 and 21). Having scrutinized the reaction conditions and a range of PNP-Ru catalysts, we concluded that the optimal conditions, with a quantitative yield of GVL, are 0.5 mol% **Ru-2**, 5 mol% Amberlyst-36, EtOH, 30 bar H_2, 120 °C, and 24 hours. We therefore continued our studies with these conditions.

We then turned our attention to the role of the Amberlyst-36 in the second hydrogenation step, *i.e.* the conversion of LA to GVL. Interestingly, as shown in Scheme 1, whereas 10 mol% Amberlyst-36 in combination with 2 mol% **Ru-2** led to 100% GVL, 20 mol% Amberlyst-36 greatly diminished the yield to 61% and 5 mol% Amberlyst-36 also leads to merely 54% GVL. Thus, this process is enhanced by 10 mol% Amberlyst-36 but hampered by additional amounts of Amberlyst-36. With 5 mol% Amberlyst-36, the optimized loading for the full cascade transformation of FAL to GVL, the acid loading seems to be insufficient to facilitate quantitative GVL production. We speculate that this observation suggests that the complete FAL conversion to GVL with 5 mol% Amberlyst-36 competes from a trade-off between FA to LA conversion by the acid and catalyst inactivation by LA. Moreover, more significant catalyst deactivation might occur when a high concentration of LA is present as in the controls experiments in Table 3.

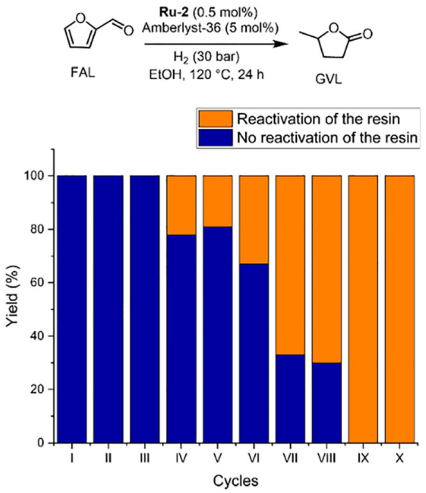
To evaluate the long-term operational stability of the catalytic system, the recyclability of the solid acid co-catalyst Amberlyst-36 was systematically investigated. Scheme 2 highlights the pronounced effect of acid-resin regeneration on the sustained catalytic performance. When Amberlyst-36 was reactivated *via* H_2SO_4 treatment after each run, quantitative yields of GVL were consistently maintained over at least ten consecutive cycles, demonstrating excellent stability and reusability of the solid acid component. In contrast, omission of the regeneration step resulted in a progressive loss of activity after the third cycle, leading to a steady decline in GVL yield. This behaviour can be attributed to gradual depletion or neutralization of Brønsted acid sites during catalysis. Periodic acid reloading effectively restores the resin's acidity, enabling sustained catalytic performance and significantly reducing waste generation. These results clearly underline the advantages of employing Amberlyst-36 over previously developed homogeneous acidic systems and demonstrate its suitability for prolonged operation under hydrogenative conditions. In fact, although the Ru-MACHO-BH catalyst constitutes the primary

Table 3 Control experiments on the hydrogenation of levulinic acid to γ-valerolactone under acidic catalytic conditions



Entry[a]	Amberlyst-36 (mol%)	GVL yield (%)[b]
1	20	61
2	10	100
3	5	54

[a] Standard reaction conditions: 0.79 mmol of LA, 2 mol% of **Ru-2** in a mixture of EtOH : H_2O 3 : 7 (2.0 mL), H_2 (30 bar), 24 h at 120 °C. [b] NMR Yield were determined by crude ^{1}H-NMR. Dimethyl sulfone was used as internal standard. Reactions are reproducible within an error margin of ±5%. The reactions were reproduced at least three times to corroborate the results.



Scheme 2 Recyclability of Amberlyst-36 in the Ru-catalysed conversion of furfural aldehyde (FA) to γ-valerolactone (GVL), with and without acid-resin reactivation.

cost contribution to the system, the use of a regenerable solid acid provides a clear economic and environmental advantage over methods requiring stoichiometric, non-recyclable homogeneous acids, which generate substantial waste and incur recurring material costs. Moreover, it constitutes in important step towards a fully recyclable system.

To assess the robustness and practical applicability of the optimized protocol, we carried out a series of scale-up experiments up to 20 mmol (1.9 g) of FAL. On this larger scale, the reaction stalled at 65–72% conversion (100% selectivity to GVL) with 0.5 mol% Ru-MACHOBH and 5 mol% Amberlyst-36 (SI, Table S6, entries 1 and 2). However, the reaction reached full conversion and quantitative amount of GVL when the catalyst loading of the organometallic catalyst was increased to 1 mol% with 20 mmol FAL (SI, Table S6, entry 3). The partial loss of conversion observed upon scale-up reflects a catalyst-loading limitation rather than catalyst deactivation, as full activity is readily restored by increasing the Ru-MACHO-BH loading (from 0.5 to 1 mol%), highlighting both the robustness and tunability of the system.

Conclusions

In summary, we have developed an efficient and highly selective catalytic system for the direct conversion of biomass-derived furfural aldehyde (FAL) to γ-valerolactone (GVL) using a homogeneous Ru-MACHO-BH catalyst in combination with a recyclable solid acid co-catalyst. Quantitative GVL yields were achieved in ethanol under hydrogenative conditions, highlighting the excellent chemoselectivity and efficiency of the approach. Notably, the use of Amberlyst-36 enables straightforward catalyst separation and reuse; periodic acid reactivation allows the resin to be recycled for at least ten consecutive cycles without loss of activity, offering a clear advantage over homogeneous acid systems in terms of sustainability and waste reduction. Scale-up experiments further demonstrate the robustness of the catalytic platform, with full conversion restored by modest adjustment of the Ru catalyst loading. Overall, this study establishes a versatile and recyclable catalytic strategy for the upgrading of furfural-derived substrates and underscores the potential of combining homogeneous hydrogenation catalysts with solid acid co-catalysts. Ongoing and future work will focus on kinetic analysis, mass-balance evaluation, and further scale-up to assess the broader applicability of this system in sustainable biomass valorisation.

Author contributions

Conceptualization: VN and MN. Methodology: VN and MN. Investigation and data curation: VN. Formal analysis: VN and MN. Visualization: VN. Writing – original draft: VN and MN. Writing – review & editing: VN and MN. Supervision: VN and MN. Funding acquisition, resources, and project administration: MN.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d6ey00082g.

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