Conversion of levulinic acid into γ-valerolactone using iron complexes as catalysts.

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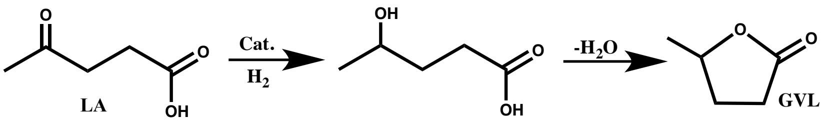
The increase of CO_2 emissions and consequently the global temperature increasing impose a new approach on dealing with the fuels and fine chemicals demand, which nowadays is mostly derived from petroleum. The use of biomass for this purpose is strongly attractive, since it is a renewable source of carbon-containing compounds. Brazil is one of the worldwide leaders in sugar cane production; however, sugar cane biomass (SCB) is mostly burned for electrical energy generation, a low efficient process. It is widely known that the acid hydrolysis of SCB furnishes levulinic acid (LA) and formic acid (FA), in almost equivalent amounts, being the first one considered a key molecule in biorefinery and the second one a valuable H_2 source. Both compounds can be applied to the synthesis of high valuable organic building blocks, like γ-valerolactone (GVL), as follows:



Aiming to obtain GVL from LA and FA, a series of iron catalyst were employed. As can be observed in Table 1, $[Fe_3(CO)_{12}]$ was the most active catalyst with 92% yield of GVL. Attempts to decrease the excess of FA, base and catalyst loading proved to be unsuccessful.

Table 1. LA conversion to GVL using Fe complexes as catalysts and water as solvent.[a]

Entry	Catalyst	Base	GVL (%)[b]
1	n.a.	n.a.	<5
2	n.a.	ImN	31
3	$[Fe_3(CO)_{12}]$	n.a.	12
4	$\mathbf{[Fe_3(CO)_{12}]}$	**ImN**	**92**
5	$[Fe(CO)_3(PPh_3)_2]$	ImN	10
6	$[Fe(CO)_5]$	ImN	24

[a] LA = 1mmol, FA = 4mmol, ImN = 4mmol, T = 180°C, t = 15h, catalyst = 4mol%. [b] Yields determined by HPLC-MS (extracted ion chromatogram by sample fortification). n.a.: no addition of catalyst or base.

After optimization of GVL production using model solutions, the conditions of entry 4 was applied for crude liquor (CL), derived from SCB acid hydrolysis containing 20% of LA, obtaining 50% of GVL yield. As the best of our knowledge, it is the first example of conversion of LA into GVL in CL without previous treatment. As conclusion, GVL was obtained in high yields in model solution and in reasonable yield in conditions mimicking biorefinery settings, using an abundant and inexpensive metal as catalyst and FA as H_2 source.

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