New catalytic processes for the conversion of biomass to levulinic acid and to γ-valerolactone

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Introduction

The utilization of renewable resources for chemicals production and energy generation will be accelerated because of the rising cost of fossil fuels. In this context the catalytic conversion of biomass to levulinic acid (LA, 4-oxopentanoic acid) appears very promising. LA has been identified as a platform chemical with interesting reactivity patterns and various potential uses for the polymer production and in other chemical industry and research fields [1]. It also can be used as solvent, antifreeze, and levulinate esters are very important derivatives: ethyl levulinate is employed as oxygenate additive for diesel fuels and in the flavouring and fragrances industry

LA can also be hydrogenated to γ-valerolactone (GVL) that can be used in perfumes and food industries as well in polymer synthesis.

LA can be obtained by acid catalyzed degradation of carbohydrates to give fructose and/or glucose which are decomposed to 5-hydroxymethyl-2-furaldehyde (HMF) and then to LA and formic acid. The yield is generally lowered by the formation of undesired solid black by-products, called humins, which can cause the clogging of the reactor [2].

Materials and Methods

The biomass conversion reaction were carried out in a 250 ml stainless steel autoclave under magnetic stirring. In a typical procedure raw biomass, water, electrolyte and acid were charged in the reactor, then it was pressurized with nitrogen and heated.

All the hydrogenation reactions were carried out in a 300 ml mechanically stirred autoclave. In a typical procedure the catalysts was inserted in the autoclave. Then the reactor was closed, evacuated up to 0.5 mm Hg and then the reaction mixture was introduced inside by suction. Then the autoclave was pressurized with hydrogen and heated.

Gas Chromatography (GC) analysis of reaction mixtures were performed on a Hewlett-Packard 5890 equipped with an HP 3396 integrator and flame ionization detector.

Results and Discussion

Many starting materials such as glucose, sucrose, starch, cellulose and biomass materials or agricultural wastes were employed to produce LA. In this context we have patented a new process for the conversion of waste biomass (paper sludge, wood wastes) which involves the use of a dilute acid in the presence of an electrolyte. The best reaction conditions such as type and concentration of acid and electrolyte, reaction temperature, duration and biomass/water ratio, are different for the different starting materials [3] and we obtained levulinic acid from raw materials with high yields without formation of solid by-produtcs.

LA was successively hydrogenated to give γ-valerolactone: this reaction rapresents a multi-step process of conversion of biomass. Up to now this reaction has been mainly performed in the presence homogeneous systems [4] or of nickel and platinum based heterogeneous catalysts [5]. Now the performances of supported commercial ruthenium catalysts have been investigated adopting mild reaction conditions. The catalytic performances are influenced by main reaction parameters, such as type of solvent and support, metal loading, temperature and pressure (table 1).

Table 1. Hydrogenation LA to GVL (cat. Ru/Al_2O_3 5 % w/w Aldrich, levulinic acid 3 g)

Run	Solvent	P-H_2 atm	T (°C)	Conversion levulinic acid (% mol)						Selectivity GVL (% mol)					
				30'	1h	2h	3h	4h	5h	30'	1h	2h	3h	4h	5h
H5	Ethanol 76 ml	70	70	5	9	18	34	47	62	70	83	95	94	96	95
H8	Ethanol 76 ml	100	50	0.2	2	8	9	13	22	10	48	48	84	86	78
H9	Methanol 76 ml	70	70	8	18	51	78	84	87	92	61	72	63	60	66
H13	Methanol 76 ml	100	50	4	5	8	10	11	15	74	77	81	82	84	79
H16	Acetic acid 76 ml	70	70	14	18	62	89	94	97	100	100	100	100	100	100
H17	Acetic acid 76 ml	100	50	6	13	29	55	87	99	100	100	100	100	100	100
H27	Acetic acid 76 ml	70	50	0.8	2	6	12	18	25	100	100	100	100	100	100

These results show very good catalytic performances even at low temperature and low pressure. We obtain the best yields using acetic acid. The optimization of the reaction conditions allows to reach very high activities working under mild conditions. A temperature as low as 50 °C is sufficient to obtain the complete conversion of the substrate to γ-valerolactone with total selectivity and in very short reaction times.

Significance

These results are very important because they show a new source for fine-chemicals from starting raw materials in a inexpensive way.

References

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