

A new two-step green process for 2,5-furandicarboxylic acid production from furfural, oxygen and carbon dioxide

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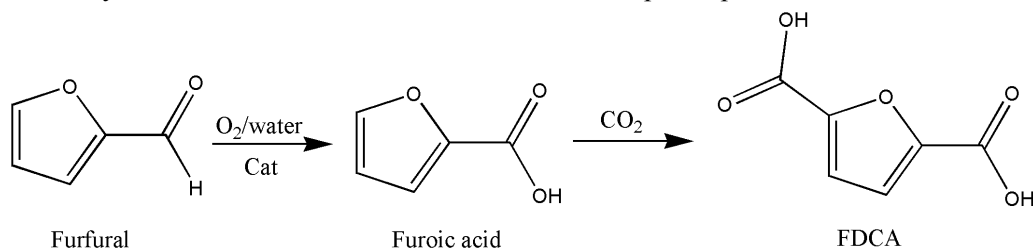
Abstract: The synthesis of 2,5-furandicarboxylic acid (FDCA) from furfural, oxygen and CO₂ via a two-step process including sequential oxidation and carboxylation reactions is reported. Firstly, furfural is oxidized with a very high yield (95%) to furoic acid under green conditions (water as solvent, O₂ as oxidant, low temperature and low pressure) on a heterogeneous gold-based catalyst. Secondly, 2-furoic acid is carboxylated with CO₂ using a mixture of molten cesium and potassium salts. The overall yield in FDCA from furfural reached 74%.

Keywords: FDCA, gold-based catalyst, furfural.

1. Introduction

In the frame of the development of bioeconomy, the chemical industry has identified a large number of biosourced platform molecules. One of the most interesting one is 2,5-furandicarboxylic acid (FDCA) due to its potential application as a building block for green polymers production¹. Currently, three methods of FDCA synthesis are described in the literature²: (i) oxidation of 5-hydroxyfurfural (5-HMF), (ii) conversion of different furanics compounds such as 5-acetoxymethyl furfural or furoic acid and (iii) dehydration of sugar acids. Until now, the best results were obtained through 5-HMF oxidation. However, its stability in acidic media is quite low and it is generally obtained from fructose, which is an edible product that must be of high purity. It has been reported that current FDCA production processes via 5-HMF are nonselective, due to the formation of unstable intermediate products³. Thus, the primary technical barrier in the large production and use of FDCA is still the development of a selective process from a biomass-derived platform molecule.

Furfural could play this role as, it is already industrially produced from non-edible renewable resources. Indeed, the oxidation of furfural can lead very selectively to 2-furoic⁴ which can then undergo C-H carboxylation with CO₂ to form FDCA^{5,6}. Herein, we report the sequential process combining the oxidation of furfural to furoic acid on a gold-based catalyst supported on hydrotalcite (Au/HT) and the further carboxylation of furoic acid to FDCA in a second step as represented in Scheme 1.



Scheme 1. FDCA synthesis via two-step sequential process.

2. Experimental

The HT support (Mg/Al molar ratios of 5:1) was prepared using a co-precipitation method from a Mg and Al nitrates aqueous solution and a Na₂CO₃ solution (Al/CO₃²⁻ molar ratio = 2 and pH of the final solution = 10.5

± 0.1). The 2 wt.% Au/HT catalyst was prepared by a deposition precipitation method using NaBH_4 and PVA as reducing and dispersing agents, respectively. The Au loading was checked by ICP-OES. XRD analysis confirmed the crystalline structure of the HT. XRF and XPS analyses were also used for further catalyst characterization. Furfural oxidation was carried out in base-free conditions in an autoclave using 500 mg of catalyst with 30 mL of an aqueous furfural solution (1.0 wt.%) under molecular oxygen (6 bar) for 0.5-2 hours in the 80-150°C range. The products were analyzed by HPLC. No furoic acid was observed in the blank test carried out without catalyst. In the second step of the process, a mixture of salts composed of furan-2-carboxylate (furoate) and carbonate with K^+ and Cs^+ cations was heated at 260–290 °C under 8 bars of CO_2 for 40 h in the absence of solvent or catalysts to form furan-2,5-dicarboxylate (FDCA^{2-}), which was subsequently protonated to produce FDCA.

3. Results and discussion

Several catalytic tests of furfural oxidation to furoic were carried out (Table 1) under different operating conditions. A full furfural conversion and 95% selectivity to furoic acid were obtained at 110 °C after 120 min of reaction. At higher temperature, the formation of secondary products was observed. At lower temperatures, the selectivity reached 94% (Table 1, Entry 4) but the furfural conversion was much lower (80%) as compared to tests carried out at 110 °C.

Table 1. Catalytic tests results obtained with Au/HT catalyst

Entry	T [°C]	Time [min]	X_{FUR} [%]	S_{FA} [%]	CB [%]
1	110	30	75	98	99
2	110	70	93	92	93
3	110	120	100	95	95
4	80	120	80	94	96
5	150	120	100	80	80

The results suggest a fast adsorption of furfural on the catalyst's surface and that the oxidation of furfural by the oxygen dissolved in water is the rate-determining step. The plausible mechanism of this first step of the process is discussed in this paper.

Concerning the second step, the carboxylation of furoic acid was performed by heating a mixture of salts composed of deprotonated form of 2-furoic acid and alkali carbonates under a CO_2 atmosphere. Using the appropriate salt composition, carbonate ion promotes the C–H carboxylation to form deprotonated FDCA. The free FDCA could be then easily obtained by protonation with strong acid (e.g. HCl) in water. Starting from the raw furoic acid obtained in the first step a 78% FDCA yield and a 92% furoic acid conversion were obtained. So, all together the overall yield of the process in FDCA from furfural is 74%.

4. Conclusions

This study demonstrates a new strategy to obtain FDCA from a platform molecule issued from non-edible biomass, namely furfural, via a two-step sequential process. The first step consists in the oxidation of furfural to furoic acid using a gold-based heterogeneous catalyst in base-free conditions. This step does not require hazardous oxidants or harsh conditions. It was shown that a 95% yield to furoic acid can be obtained working in water and using oxygen as oxidant. In the second step, very good results were also obtained for the carboxylation of furoic acid with CO_2 to finally get an overall yield in FDCA from furfural of 74%.

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