DOI: 10.1002/cssc.201200652

Catalytic Conversion of Furfural into a 2,5-Furandicarboxylic Acid-Based Polyester with Total Carbon Utilization

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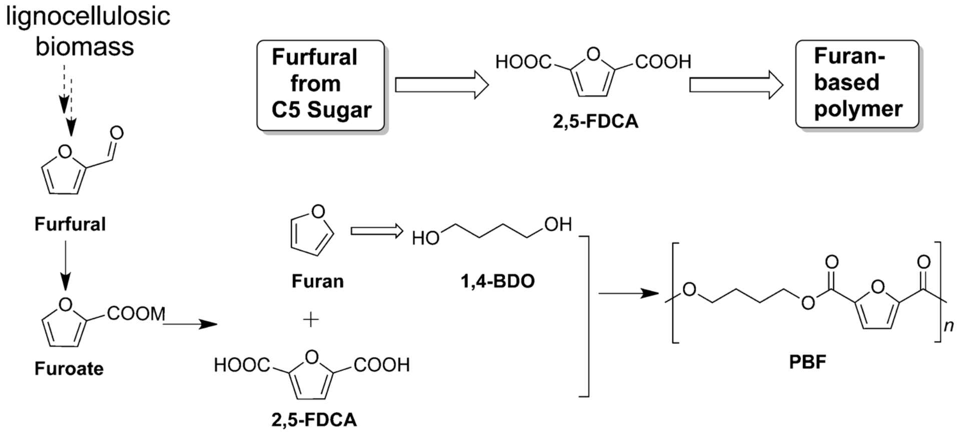
The conversion of renewable biomass resources into fuels, polymers, and fine chemicals provides solutions for the growing shortage of fossil resources, environmental pollution, and a possible crisis in energy supply.[1] In particular, the C$_6$ and C$_5$ sugars in lignocellulosic biomass (e.g., D-glucose, D-fructose, D-xylose) are promising precursors for the production of synthetic polymers. Recently, a number of examples have demonstrated that sugars and related platform molecules obtained from sugars can be converted into a series of polymer monomers and polymers. For example, Holm and co-workers have reported the preparation of lactic acid (the monomer for polylactic acids) from fructose and glucose.[2] Heeres and co-workers have reported the conversion of a biomass-derived platform molecule 5-hydroxymethylfurfural (5-HMF, the dehydration product of C$_6$ sugars) into the nylon-6 monomer caprolactam.[3] Furthermore, Thomas and co-workers have reported the synthesis of alternating polyesters from dicarboxylic acids (the products of carbohydrate fermentation).[4]



Scheme 1. Multistep conversion of furfural into the 2,5-furandicarboxylic acid-based polyester PBF.

Furan-based polymers, which may be produced from saccharides, have the potential to replace some petroleum-based polymers.[5] In particular, 2,5-furandicarboxylic acid-based polyesters represent one of the most important types of furan-based polymers.[6,7] For example, poly(ethylene 2,5-furandicarboxylate) (PEF) is considered to be a potential substitute for poly(ethylene terephthalate) (PET).[8] The key monomer 2,5-furandicarboxylic acid (2,5-FDCA) is a promising biobased platform molecule.[1c,9] Until now, the only developed route for the production of 2,5-FDCA involves the selective oxidation of 5-HMF.[10] Although the preparation of 5-HMF from glucose and cellulose has been extensively studied,[11] the large-scale commercial production of 5-HMF has been hampered by several difficulties (e.g., the cost of the process,[8a] the low efficiency of the glucose-to-fructose transformation,[12,13] and the difficulty encountered in the isolation of 5-HMF[14]).

On the other hand, furfural, which is a bulk biomass-based chemical with a global annual production of 280 000 tonnes,[15] is readily produced from D-xylose in xylan or hemicellulose.[16] It can be converted into a variety of derivatives with potential applications as fuels, polymers, pharmaceutical intermediates, and pesticides.[17] It is therefore of interest to develop a route to produce of 2,5-furandicarboxylic acid-based polyester from furfural, and thereby avoid the short supply of 5-HMF.

Herein, we report a multistep catalytic conversion of furfural into poly(butylene 2,5-furandicarboxylate) (PBF) by disproportionation of furoate to furan and 2,5-furandicarboxylate (Scheme 1). The route includes four steps: (1) catalytic oxidation of furfural into furoate; (2) catalytic disproportionation of furoate to furan and 2,5-furandicarboxylate; (3) catalytic hydrogenation and hydrolysis of furan to 1,4-butanediol (1,4-BDO); and (4) polymerization of 1,4-BDO with 2,5-FDCA to PBF. The key step of the route is the selective conversion of furoate into furan and 2,5-furandicarboxylate, which provides an important linkage between commercialized biobased furfural and the furan-based polymer monomer 2,5-FDCA. Compared to the oxidation method for the production of 2,5-FDCA from 5-HMF, the furfural route is more practical due to the abundant supply of the feedstock. Furthermore, the key monomer 1,4-BDO can be produced from furfural, leading to total carbon utilization of furfural.

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Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201200652.

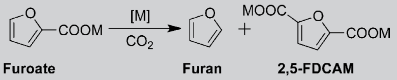
The first step of our route is the catalytic oxidation of furfural into furoate. Although a number of oxidants (e.g., $KMnO_4$) could be used for this oxidation, catalytic aerobic oxidation is more suitable for biomass conversion and therefore explored here. This catalytic aerobic oxidation of furfural to furoate has previously been reported, employing supported metal as catalyst.[18] The oxidation process was performed in aqueous phase under alkaline conditions, using air or oxygen as oxidant with a series of heterogeneous catalysts, including nanometer-scale particles of CuO, CuO-Ag_2O, Pt/C, Pd/C, Pt/C/CuO-Ag_2O, and Pd/C/CuO-Ag_2O.[18] In our experiments, we found that nanoscale CuO (furfural/KOH = 1:1, 40 wt% KOH, 30 wt% of catalyst intake, 60 °C, 30 min, air) gave 93% selectivity to furoate at 100% furfural conversion.

The second step of the route is the catalytic disproportionation of furoate to furan and 2,5-furandicarboxylate. Baecke and other groups have reported the preparation of dipotassium terephthalate in the presence of catalysts such as cadmium or zinc salts by reacting dipotassium phthalate or potassium benzoate at 400–450 °C with the carboxyl transposition reaction,[19] known as the Henkel reaction. The Henkel reaction has been used for the industrial production of terephthalic acid and 2,6-naphthalene dicarboxylic acid.[20] A similar reaction using furoate as the substrate could be envisaged to generate furan and 2,5-furandicarboxylate. After the first step of the catalytic oxidation of furfural to furoate, the solid furoate was obtained by filtering the catalyst from the solution and removing water without acidification. In a subsequent step, the catalyst was added to the solid furoate for solid-phase disproportionation reaction to produce furan and 2,5-furandicarboxylate. We screened different catalysts and studied the effects of the reaction temperature and reaction time (Table 1).

To avoid the decomposition of furoate and 2,5-furandicarboxylate under the reaction conditions, the decomposition temperatures of potassium furoate and dipotassium 2,5-furandicarboxylate were determined by thermogravimetric analysis (TGA). The TGA curves showed that the substrate and product are stable below 330 °C. First, a control experiment showed that almost no conversion of furoate took place without catalyst (Table 1, entry 1). Then the disproportionation of furoate was tried with Henkel reaction catalysts of zinc salts and cadmium salts (entries 2 and 3). Cadmium chloride showed almost no catalytic activity at 280 °C, while zinc chloride showed a significant catalytic activity. Copper salts have been shown to catalyze the decarboxylation of aromatic carboxylate under homogeneous conditions,[21] but showed no selectivity to 2,5-FDCA here (entry 4). Two Lewis-acid catalysts and a transition metal catalyst (i.e., nickel salt) were tested, also, but did not give good results (entries 5–7). According to previous studies of the Henkel reaction, the anion of the catalyst has a pronounced impact on the conversion.[19] Zinc oxide and zinc acetate (entries 8 and 9) were used as catalysts, but no products could be detected (zinc acetate was in a molten state at the reaction temperature).

Considering the possible mechanism of the Henkel reaction,[22] the disproportionation reaction comprises an initial decarboxylation and a subsequent carboxylation. Therefore, carbon dioxide may be involved in the reaction. To elucidate the effect of CO_2, an additional experiment was performed without addition of dry ice (Table 1, entry 10). The result showed that CO_2 has a beneficial effect on reactivity and selectivity. Furthermore, solid acid and base were added as additives, but their effect on the results was found to be detrimental (entries 11 and 12). Finally, sodium furoate was tried at 250 °C for 180 min, and similar results were obtained (entry 13).

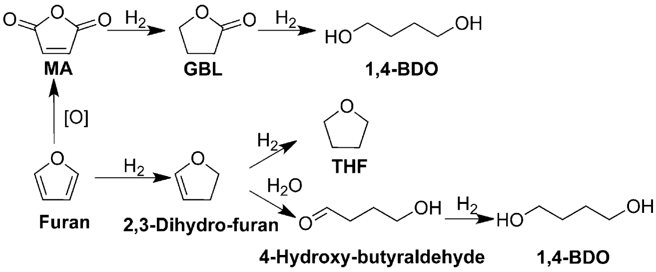
Table 1. Disproportionation of furoate to furan and 2,5-furandicarboxylate.[a]



Entry	Cat	T [°C]	t [min]	FCAM conv. [%]	Selectivity to 2,5-FDCA [%]
1	–	280	180	1	0
2	$ZnCl_2$	280	30	56	46
3	$CdCl_2$	280	30	23	0
4	$CuCl_2$	280	30	18	0
5	$LaCl_3$	280	30	3	0
6	$SnCl_2$	280	30	15	11
7	$NiCl_2$	280	30	6	0
8	ZnO	280	30	2	0
9	$Zn(OAc)_2$	280	30	14	0
10[b]	$ZnCl_2$	280	30	8	17
11[c]	$ZnCl_2$	280	30	48	29
12[d]	$ZnCl_2$	280	30	27	19
13[e]	$ZnCl_2$	250	180	21	73
14	$ZnCl_2$	280	180	85	15
15	$ZnCl_2$	270	180	75	44
16	$ZnCl_2$	260	180	67	67
17	$ZnCl_2$	250	180	61	86
18	$ZnCl_2$	240	180	55	76
19	$ZnCl_2$	230	180	35	65
20	$ZnCl_2$	220	180	18	46
21	$ZnCl_2$	250	30	9	7
22	$ZnCl_2$	250	60	29	71
23	$ZnCl_2$	250	90	37	77
24	$ZnCl_2$	250	120	38	77
25	$ZnCl_2$	250	150	45	76
26	$ZnCl_2$	250	240	69	76

[a] The potassium furoate (FCAK) 2 g, cat 0.2 g, dry ice 1.0 g, the conversion of furoate and the yield of 2,5-FDCA were determined by HPLC. [b] Without dry ice. [c] 0.1 g HZSM-5 was added. [d] 0.01 g NaOH was added. [e] The substrate is sodium furoate (FCANa).

The reaction temperature was further optimized (220∼280 °C, Table 1, entries 14–20) while extending the reaction time to 180 min. With the decrease of the reaction temperature, the conversion of furoate gradually decreased. Meanwhile, the selectivity to 2,5-FDCA increased at first and then dropped. The highest selectivity to 2,5-FDCA (86%) was achieved at 250 °C with a conversion of 61% (entry 17). A longer reaction time led to an increase in furoate conversion at 250 °C with an unchanged selectivity to 2,5-FDCA (30∼240 min, entries 21–26). The other product furan was in the gas state under the reaction conditions and gaseous products were collected and analyzed by GC after the reaction. GC analysis revealed no gaseous products other than CO_2 and furan.



Scheme 2. Routes for the conversion of furan into 1,4-butanediol.

For the third step of the conversion of furan to 1,4-butanediol (1,4-BDO), we propose two routes (Scheme 2). One route comprises three steps. First, furan is catalytically oxidized to maleic anhydride (MA), which is then hydrogenated to 1,4-BDO in two steps [hydrogenation to butyrolactone (GBL) and then hydrogenation to 1,4-BDO]. The two-step hydrogenation of MA to 1,4-BDO is currently a mature technology in industry.[23] Thus, the only step missing from our proposed route is the catalytic oxidation of furan to MA. Based on the industrial catalytic oxidation of *n*-butane to MA, vanadium-containing catalysts ($VOPO_4$, $VOHPO_4$, and VPO) were selected in our experiments, with air as oxidant. The highest selectivity to MA (48 %) was obtained when using VPO as catalyst at 74 % furan conversion, at 400 °C.

Because the selectivity to the product 1,4-BDO was not high in the first route, another route was tested (Scheme 2). This route involves direct hydrogenation of furan into 1,4-BDO,[24] and Scheme 2 shows the possible pathway of catalytic hydrogenation and hydrolysis of furan to the 1,4-BDO. The main byproducts were tetrahydrofuran (THF) and *n*-butanol. A range of catalysts (Pt/C, Ru/C, Pd/C, Raney-Ni, Ru-Ni/C and Ru-Ni/Si-Al) was explored in a batch autoclave at 160 °C and 30 bar hydrogen pressure, with water as solvent. The main product was THF and the yield of target product 1,4-BDO was less than 5 %. A small quantity of Brønsted acid (H_2SO_4) as catalytic additive was added to promote the ring-opening hydrolysis of 2,3-dihydro-furan, but the results were unsatisfactory (less than 2 % yield of 1,4-BDO). Recently, a number of reports on rhenium-containing catalysts applied to the hydrogenolytic ring-opening of furan and THF have appeared.[25] Thus, the hydrogenation of furan was carried out by using bimetallic catalysts containing Re. The best result was obtained when using Re–Ru/C (4 % Re and 1 % Ru) at 160 °C under a hydrogen pressure of 3 MPa for 3 h, giving a maximum selectivity to 1,4-BDO of 70 % at 99 % furan conversion. The remaining byproducts included 25 % of THF and a small amount of *n*-butanol. The final step was polycondensation of 2,5-FDCA and 1,4-BDO to PBF. The preparation and characterization of furan-based polyester from 2,5-FDCA and diol (e.g., ethylene glycol, 1,3-propylene glycol, and 1,4-BDO) have been reported.[26,27]

In conclusion, a multistep route for the catalytic conversion of furfural into 2,5-furandicarboxylic acid-based polyester PBF with total carbon utilization is demonstrated. The catalytic oxidation of furfural into furoate is easily achieved, with a selectivity of 93 % at 100 % furfural conversion. The best results of catalytic disproportionation of furoate to furan and 2,5-furandicarboxylate are obtained with a selectivity to 2,5-FDCA of 86 %, at 61 % furoate conversion. This demonstrates a new pathway of converting furfural, a bulk biomass-based chemical, into 2,5-FDCA, a key monomer for 2,5-furandicarboxylic acid-based polyesters, with a good overall selectivity (80 % for the two-step process). Moreover, furan is converted into 1,4-BDO at a very high selectivity of 70 %, at 99 % furan conversion. The furan-based polyester PBF is thus prepared from 2,5-FDCA and 1,4-BDO with total carbon utilization of furfural. This route demonstrates an important, yet so far neglected strategy of linking a platform molecule from C_5 sugars (furfural) to one from C_6 sugars (2,5-FDCA). Further studies should enable to open up a new pathway for biorefineries.

Experimental Section

Catalytic Oxidation of Furfural to Furoate: A 40 % KOH solution and 6 g of furfural (distilled before use) were added dropwise to a reaction flask containing 2 g of copper oxide nanoparticles at 60 °C (furfural/KOH = 1:1). Air was passed into the reaction mixture at the same time (40 mL min^{-1}). The mixture was stirred for 10 min after adding KOH and furfural. After reaction, the mixture was filtrated to remove the catalyst and the filtrate was analyzed by HPLC. The filtrate was concentrated in vacuo to remove water and the crude material was dried in vacuo at 50 °C.

Catalytic Disproportionation of Furoate: 2 g of furoate, 2 g of catalyst, and 1 g of dry ice were mixed and added into a 25 mL stainless steel autoclave. The reactor was stirred and heated to a certain temperature for a setting time (see Table 1). After cooling, the gas product was collected for GC analysis, and the solid product was poured into water and analyzed by HPLC.

Hydrogenation of Furan to 1,4-BDO: 1 g of furan, 0.5 g of catalyst, a certain quantity of additive and 5 mL of water were added into a 25 mL stainless steel autoclave (Parr). The reactor was flushed three times with hydrogen and pressurized to 3 MPa. The reaction mixture was stirred and heated to 160 °C for 3 h. After cooling to room temperature, the pressure was released carefully and the products were analyzed by GC.

Acknowledgements

This work was supported by the National Basic Research Program of China (2012CB215305), the National Natural Science Foundation of China (21172209), and the Chinese Academy of Science (KJCX2-EW-J02).

Keywords: biomass · furfurals · polymers · renewable resources · synthetic methods

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Received: September 2, 2012
Revised: October 29, 2012