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A scalable carboxylation route to furan-2,5-dicarboxylic acid†

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Furan-2,5-dicarboxylic acid (FDCA) is a biomass-derived diacid that can be used to make polymers including polyethylene furandicarboxylate (PEF), a highly attractive substitute for petroleum-derived polyethylene terephthalate (PET). Current FDCA syntheses require edible fructose as the feedstock, entail a difficult oxidation step that generates undesirable aldehyde impurities, and have moderate yields. As an alternative, carbonate-promoted C–H carboxylation enables the synthesis of FDCA from 2-furoic acid and CO_2. This route is potentially advantageous because 2-furoic acid is made from furfural, a feedstock produced commercially from inedible lignocellulosic biomass, and it obviates late-stage oxidation. In the carboxylation reaction, salt mixtures composed of alkali furan-2-carboxylate (furoate) and alkali carbonate (M_2CO_3) are heated under CO_2 in the absence of solvent or catalysts to form furan-2,5-dicarboxylate ($FDCA^{2-}$), which is subsequently protonated to produce FDCA. Previously, high yields were achieved on small-scale reactions using caesium furoate and Cs_2CO_3. In this work, we investigate the carboxylation reaction using alkali furoate/M_2CO_3 salts containing cation blends and describe reaction conditions that provide high yields on a preparative scale. We show that the carboxylation proceeds efficiently with K^+/Cs^+ blends that have a high K^+ content (up to 4 : 1 K^+ : Cs^+). Removing H_2O, which is a by-product of the reaction, is important for suppressing decomposition pathways. The accumulation of the $FDCA^{2-}$ product inhibits the reaction. Integrating these lessons, we demonstrate the carboxylation of furoate on a 1 mol scale using a fixed-bed flow reactor with 89% isolated yield of pure FDCA upon protonation.

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Introduction

Polyethylene terephthalate (PET) and polyethylene furandicarboxylate (PEF) were both originally patented nearly 70 years ago.[1,2] PET has since grown to become a $>10^7$ ton per year polymer, with applications in rigid packaging, fibres, and films. This growth was made possible by the development of scalable syntheses of purified terephthalic acid (PTA), the diacid monomer, which is made by oxidation of petroleum-derived *para*-xylenes.[3] PEF is an attractive replacement for PET because its diacid monomer, furan-2,5-dicarboxylic acid (FDCA), is derived from biomass,[4] which provides an opportunity to produce a polymer with a much lower greenhouse gas (GHG) footprint.[5] In addition, PEF has superior gas barrier and mechanical properties compared to PET for certain packaging applications such as bottled beverages.[6–8]

PEF and other FDCA-based polymers have attracted increased interest in the past several years.[9–11] A number of synthetic routes to FDCA and its derivative dimethylfurandicarboxylate (DMFD) have been advanced to pilot-scale production and plans have been announced for the first commercial scale plant.[12] All of these routes use a C_6 sugar (hexose) as the feedstock and follow a similar synthetic strategy. The hexose is first dehydrated to form hydroxymethyl furfural (HMF), which is then oxidized to FDCA (Scheme 1). DMFD is made either by esterifying FDCA or etherifying HMF to form methoxymethyl furfural (MMF) and then oxidizing it in methanol.[13] This basic approach—hexose dehydration followed by oxidation—has several drawbacks. In their current form, these syntheses require edible fructose as the hexose feedstock. Edible fructose has a large GHG footprint[5] and its use for commodity-scale plastic production would compete with food production. Using hexoses derived from lignocellulosic biomass would avoid these issues, but thus far it has proven very challenging to obtain FDCA economically from lignocellulose-derived hexoses.[14] Another major drawback is the difficulty of oxidizing HMF to FDCA (or MMF to DMFD). This reaction is typically performed under highly corrosive conditions in acetic acid solvent,[15–17] similar to the conditions used to oxidize *para*-xylenes to terephthalic acid.[3] Moreover, even under optimized conditions, the reaction also forms alde-

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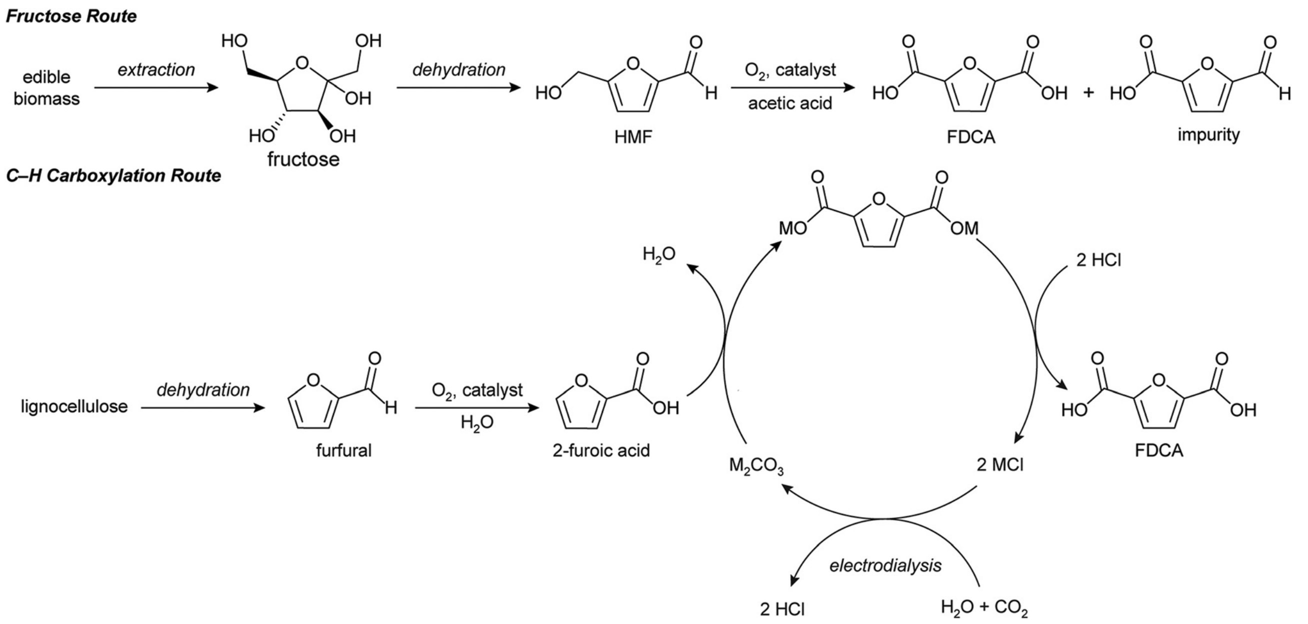

Scheme 1 (Top) Route for producing FDCA from edible biomass. A common impurity of the oxidation of hydroxymethylfurfural (HMF) is the incomplete oxidation product, 5-formyl-2-furoic acid. (Bottom) Diagram depicting the overall scheme for producing FDCA from lignocellulose through furfural using CO_3^{2-}-promoted C–H carboxylation. Recovery of the alkali cations is achieved by protonation of the FDCA salt and bipolar membrane electrodialysis of the resulting alkali chloride salt.

hyde impurities that cause chain terminations during polyester synthesis and discolour the polymer. Removing these impurities requires a separate chemical step—either hydrogenation or a second oxidation.[18,19] While much progress has been made in advancing FDCA and DMFD synthesis toward commercial production, alternative routes that avoid these drawbacks are highly desirable.

We recently described a C–H carboxylation reaction that makes it possible to synthesize FDCA from 2-furoic acid and CO_2 in high yield without energy-intensive reagents or transition metal catalysts.[20] This reaction is performed by heating a salt mixture composed of alkali furoate (the deprotonated form of 2-furoic acid) and alkali CO_3^{2-} under a CO_2 atmosphere. With the appropriate salt composition (see below), CO_3^{2-} promotes the C–H carboxylation to form furan-2,5-dicarboxylate ($FDCA^{2-}$). Protonation with strong acid (*e.g.* HCl) in water yields precipitated FDCA product and an aqueous salt solution (*e.g.* MCl) (Scheme 1). The stoichiometric base and acid consumed in this synthesis can be regenerated by subjecting the salt solution to bipolar membrane electrodialysis.[21,22]

This carboxylation route to FDCA has a number of potential advantages over conventional hexose-based routes. First, 2-furoic acid is made from furfural, a compound that has been produced from lignocellulosic biomass industrially for almost a century.[23,24] Furfural is made by depolymerizing and dehydrating the pentose-rich hemicellulose component of lignocellulose, which is much easier to process than the hexose-rich cellulose component. Multiple biomass waste streams have been used for furfural production, including corncobs, bagasse, and the hemicellulose waste of wood pulp production.[23] Second, oxidizing furfural to 2-furoic acid is easier than oxidizing HMF to FDCA. Although 2-furoic acid is not currently synthesized on a commodity scale, multiple reports describe high-yielding oxidations of furfural or furfuryl alcohol to 2-furoic acid using O_2 under relatively mild conditions (*e.g.* 50 °C, 1 bar).[25–28] Lastly, CO_3^{2-}-promoted C–H carboxylation requires no solvent or transition metal catalysts and installs the final carbon in the appropriate oxidation state.

Utilizing this chemistry to supply FDCA for polymer production requires finding carboxylation conditions that are amenable to very large-scale reactions with minimal by-products and facile purification. In our previous work, carboxylation reactions were performed by heating mixtures of caesium furoate and Cs_2CO_3 under static CO_2 pressure.[20] High yields of up to 89% for $FDCA^{2-}$ were obtained on a 1–10 mmol scale, but a diminished yield of 71% was obtained upon scaling to 100 mmol. Isotope exchange experiments suggested that the reaction proceeds by deprotonation of the C–H bond at the 5 position of 2-furoate by CO_3^{2-} to form a carbanion that undergoes a C–C bond-forming reaction with CO_2. CO_3^{2-} is ordinarily incapable of deprotonating this C–H bond (pK_a 35),[29] but in a solvent-free caesium furoate/Cs_2CO_3 mixture there is a high concentration of Cs^+ cations that can stabilize the anionic species. At the temperatures required for carboxylation, the mixture is semi-molten, providing sufficient ion mobility for the reaction to occur. We attributed the diminished yield upon scaling to 100 mmol to a reduced surface area-to-volume ratio, which impedes transport of CO_2 into the salt and removal of H_2O. In the absence of other additives, alkali furoate/alkali CO_3^{2-} mixtures with a single cation other than Cs^+ do not

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undergo C–H carboxylation, suggesting that these salts remain in an unreactive crystalline form at elevated temperatures. However, we demonstrated that furoate carboxylation could be achieved in small-scale (1 mmol) reactions with all K^+ salts by combining potassium furoate/K_2CO_3 with a potassium carboxylate co-salt (*e.g.* potassium isobutyrate) to increase ion mobility at elevated temperatures.[20]

In this work, we investigate furoate carboxylations with salts containing cation mixtures and develop conditions for mole-scale carboxylation in high yield using fixed-bed flow reactors. We show that carboxylation proceeds efficiently with alkali furoate/M_2CO_3 salts if K^+/Cs^+ cation mixtures are used, even with high $K^+ : Cs^+$ ratios. This advance enables carboxylation with a reduced Cs^+ loading without requiring a co-salt. Although the cations would be recycled in a practical application, reducing the Cs^+ loading is desirable because the amount of Cs^+ salts mined annually is relatively low.[30] More importantly, alkali furoate/M_2CO_3 salts with K^+/Cs^+ mixtures do not undergo a bulk phase transition to a molten phase, which facilitates scale-up. Using a fixed-bed reactor under flowing CO_2, we demonstrate furoate carboxylation with K^+/Cs^+ salts on a 1 mol scale with 89% isolated yield for FDCA upon acidic work up.

Results

Small-scale reactions

The synthesis of $FDCA^{2-}$ *via* C–H carboxylation is performed by heating furoate and CO_3^{2-} under CO_2. The yield and reaction rate depend on the precise composition and morphology of the salt mixture, the temperature, and CO_2 mass transport. To assess whether pure Cs^+ salts could be substituted with cation blends, we initially surveyed the reaction on an analytical scale (0.5 mmol substrate) using different $K^+ : Cs^+$ ratios. To prepare the solid reactants, 2-furoic acid was added to an aqueous K_2CO_3/Cs_2CO_3 solution (1.25 total molar equivalents of CO_3^{2-}) in a glass vial and dried to a solid, which is composed of 2-furoate and 0.75 equivalents of residual CO_3^{2-}. This material was then heated in a vial block with a constant purge of CO_2 through the headspace for 17 h. The product mixture was analysed directly by NMR using an internal standard. The yields are far from optimal in this vial block reactor (see below), but the setup permits rapid initial assessment of the effects of varying the salt composition.

Fig. 1 shows the $FDCA^{2-}$ yield as a function of temperature for several $K^+ : Cs^+$ ratios. As a reference point for these vial block reactions, the yield with only Cs^+ (caesium furoate + Cs_2CO_3) reached a maximum of 71% at 260 °C. Reactions with only K^+ in the absence of co-salts (potassium furoate + K_2CO_3) do not form any $FDCA^{2-}$ regardless of the temperature (data not shown). However, K^+/Cs^+ blends containing a high proportion of K^+ (1 : 1 to 4 : 1 $K^+ : Cs^+$) gave 60–70% yield of $FDCA^{2-}$. The optimal temperature for the K^+/Cs^+ reactions increased with the K^+ content. The mass balance of the reactions was composed of unreacted furoate and decomposition products. The decomposition products consist mostly of insoluble char and smaller amounts of acetate and malonate.

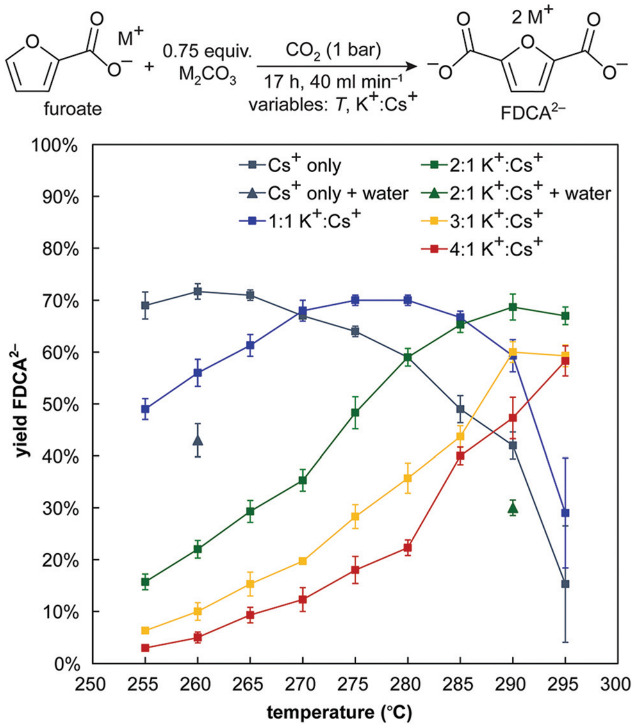

Fig. 1 The C–H carboxylation of the 5 position of furoate promoted by CO_3^{2-} at various temperatures and ratios of $K^+ : Cs^+$. Reactions denoted "+ water" had CO_2 gas streams that were pre-saturated with water before introduction to the reactions. All yields were determined by comparison to an internal standard by NMR. Reactions were performed in triplicate and the error bars represent the standard deviation.

The cation composition affects the morphology of the salt under the reaction conditions. In the all Cs^+ reaction, the salt mixture is partially molten at the temperatures where good yields are observed. With a K^+/Cs^+ blend, however, the salts do not appear to undergo a bulk phase transition. The ability to synthesize $FDCA^{2-}$ without forming a bulk molten solution provides flexibility in reactor design and facilitates scale-up (see below).

To gain insight into the origin of the decomposition products, we first assessed the effect of the cation composition on the thermal stability of the substrate and product in the absence of CO_2. Heating furoate and 0.75 equivalents of CO_3^{2-} under N_2 for 6 h at 265 °C to 295 °C caused decomposition to similar products seen in the carboxylation reaction (Fig. 2). The amount of decomposition increased with temperature and with the Cs^+ content of the salt mixture. Thus, the higher the K^+ loading, the greater the intrinsic thermal stability of furoate. Regardless of the cation composition, the amount of decomposition observed under N_2 was comparable to or greater than the amount of $FDCA^{2-}$ produced under CO_2 at the same temperature. For example, at 285 °C, the 2 : 1 $K^+ : Cs^+$ blend produced 63% $FDCA^{2-}$ under CO_2 after 17 h, whereas >90% of the furoate decomposed after only 6 h under N_2. This

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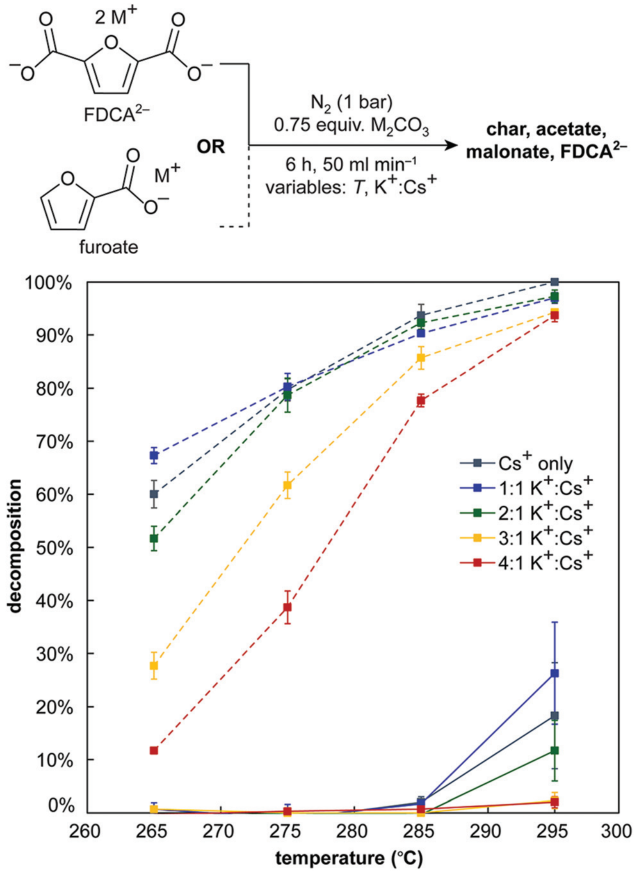

Fig. 2 The thermal decomposition of the furoate (dashed line) and $FDCA^{2-}$ (solid line) salts under N_2 atmospheres in the presence of CO_3^{2-} at various temperatures and ratios of $K^+ : Cs^+$. The percent decomposition was determined by comparison to an internal standard by NMR. Reactions were performed in triplicate and the error bars represent the standard deviation.

result suggests that CO_2 greatly curtails the rate of furoate decomposition, in addition to making the carboxylation reaction possible. In contrast to furoate, $FDCA^{2-}$ showed good thermal stability under N_2 with all cation compositions up to 285 °C (Fig. 2). Some decomposition was observed at 295 °C, with a similar cation dependence as seen for the substrate. The decomposition products observed during carboxylation therefore arise from furoate decomposition rather than the $FDCA^{2-}$ product.

Water is a by-product of CO_3^{2-}-promoted C–H carboxylation. We hypothesized that water could be deleterious to furoate carboxylation by providing a source of hydroxide ions that cause decomposition *via* nucleophilic attack on furoate. To test this hypothesis, the all Cs^+ and the $2:1\ K^+ : Cs^+$ carboxylations were repeated at their optimal temperatures using a CO_2 stream passed through a water bubbler to hydrate the gas before flowing into the glass vials (Fig. 1, "+ water" conditions). Under these conditions, the $FDCA^{2-}$ yield was reduced from 71% to 41% in the all Cs^+ reaction and from 70% to 31% in the $2:1\ K^+ : Cs^+$ reaction. Analysis of the mass balance for the all Cs^+ reaction indicated that H_2O mostly slowed down $FDCA^{2-}$ synthesis without substantially accelerating decomposition (*i.e.* both yield and furoate conversion were reduced). In contrast, H_2O greatly increased the decomposition products for the $2:1\ K^+ : Cs^+$ reaction. This result suggests that removing the H_2O by-product is important for suppressing decomposition during carboxylation when cation blends are used, which is further supported by experiments in the fixed-bed reactor (see below).

We next probed the kinetics of carboxylation in the vial block reactor by performing a time course experiment. A set of identical reaction mixtures with $2:1\ K^+ : Cs^+$ was heated under CO_2 at 285 °C and individual reactions were stopped at different reaction times for analysis (Fig. 3). The $FDCA^{2-}$ yield rose steadily to 50% in the first 5 h, but thereafter the reaction slowed dramatically, requiring an additional 12 h to reach 63% yield. Quantification of the substrate consumption indicated that 14% decomposed in the first 5 h and an additional 10% decomposed over the next 12 h. The greatly attenuated substrate decomposition relative to experiments under N_2 (Fig. 2) confirms that CO_2 inhibits the decomposition pathways. Additional time course experiments were performed with different amounts of CO_3^{2-}. Increasing the CO_3^{2-} loading beyond 0.75 equivalents increased the initial reaction rate, but did not eliminate the sharp drop in the reaction rate after

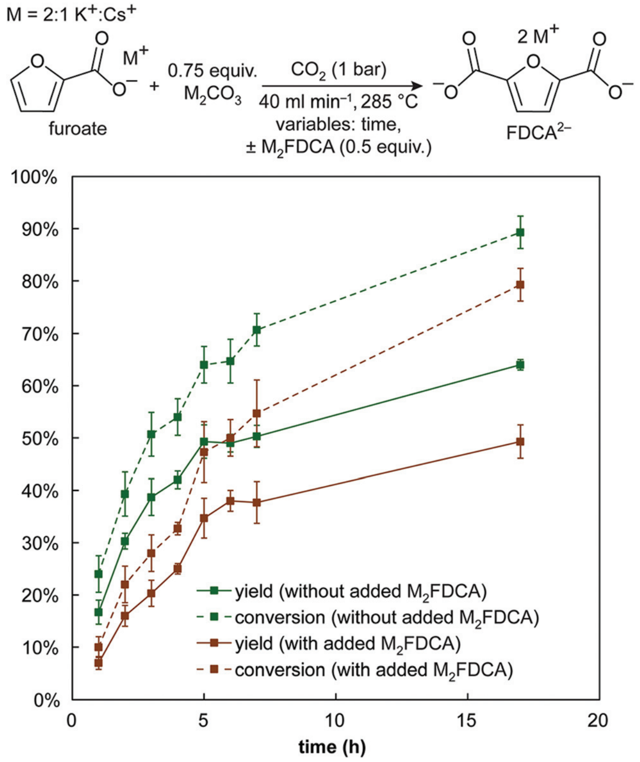

Fig. 3 The kinetics of the C–H carboxylation of the 5 position of furoate promoted by CO_3^{2-} with or without the addition of 0.5 equivalents of $FDCA^{2-}$. All yields were determined by comparison to an internal standard by NMR. Reactions were performed in triplicate and the error bars represent the standard deviation.

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~50% $FDCA^{2-}$ formation (Fig. S8†). To see if $FDCA^{2-}$ itself slows the furoate carboxylation, a time course was performed using a salt mixture spiked with 0.5 equivalents of $FDCA^{2-}$. Under these conditions, the synthesis rate and yield of $FDCA^{2-}$ were reduced, and furoate decomposition increased (Fig. 3). This experiment shows that the build-up of $FDCA^{2-}$ slows down the carboxylation of remaining furoate, either by impeding CO_2 transport or slowing the rate of deprotonation.

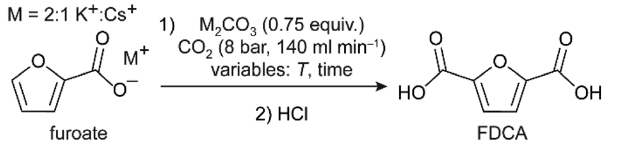
Fixed-bed flow reactor

The vial block reactor provides relatively poor gas transport because CO_2 can only be flowed through the headspace above the solid reactants. To determine whether increased contact between the salt mixture and CO_2 improves the yield, we assembled a fixed-bed flow reactor. In brief, the reactor consists of a temperature-controlled stainless steel tube (the reaction vessel) connected to a CO_2 pre-heating apparatus (see ESI† for details). The reactor accommodates 8 bar CO_2 at elevated temperature and flow rates up to several hundred ml min^{-1}. For fixed-bed flow experiments, we used industrial grade CO_2 (99.5%). We first evaluated the effects of static *vs.* flowing CO_2 on a 10 mmol scale for different cation compositions (Table 1). The solid reactants were prepared as described above and transferred to the reaction vessel as dry powders. The reactions were performed at 265 °C to 300 °C under 8 bar CO_2 for 14 h with either no flow or a flow rate of 140 ml min^{-1}. With all Cs^+, the $FDCA^{2-}$ yield was 91% in the absence of flow at 265 °C. This result is consistent with the high carboxylation yield observed on the 10 mmol scale with all Cs^+ in a Parr reactor.[20] For reactants with 1 : 1 to 4 : 1 $K^+ : Cs^+$, however, the $FDCA^{2-}$ yield was only 22%–56% under static conditions and large amounts of decomposition products were formed. Upon switching from static to flowing CO_2, the $FDCA^{2-}$ yields increased to 71%–79% and decomposition products were suppressed. Under flowing conditions, water formed during the reaction is stripped away. Since water is deleterious to the carboxylation reaction, the boost in yield seen under flowing conditions can be attributed to water removal. Additionally, flow forces CO_2 through the solid material, which may expose salt particles to CO_2 more efficiently than under static conditions. Remarkably, flowing conditions gave a 56% yield of $FDCA^{2-}$ for a reaction with a 20 : 1 $K^+ : Cs^+$ ratio (Table 1), providing proof-of-concept for the ability to perform carboxylation with cation blends that have very low Cs^+ content.

Preparative-scale reactions

Fixed-bed flow conditions were used to evaluate the carboxylation on preparative scales. Experiments were performed with 2 : 1 $K^+ : Cs^+$ blends using the reactor design described above with larger reaction vessels to accommodate the increased reactant volumes (see ESI†). At the conclusion of the reactions, the solid products were dissolved in H_2O, filtered to remove insoluble by-products, and acidified with HCl to precipitate FDCA. Isolated yields are reported for dry, purified FDCA (Table 2). The reaction was first attempted on a 100 mmol scale at 285 °C with 140 ml min^{-1} CO_2 at 8 bar. After a 24 h

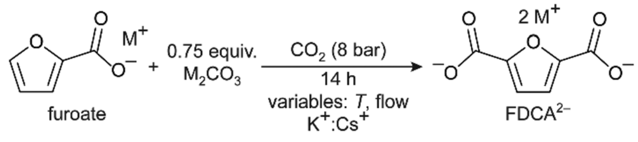
Table 2 Preparative-scale CO_3^{2-}-promoted C–H carboxylation of furoate



Scale	*T*	Ramp rate[a]	Soak time[a]	FDCA[b]	Starting material
100 mmol	285 °C	N/A	24 h	66%	0%
100 mmol	260–285 °C	2 °C h^{-1}	24 h	86%	3%
1 mol	260–285 °C	2 °C h^{-1}	24 h	89%	2%

[a] The temperature was ramped from 260 °C to 285 °C at the specified ramp rate and then held (soaked) at 285 °C for 24 h. [b] Isolated yield of the diacid.

Table 1 Effect of flowing CO_2 on CO_3^{2-}-promoted C–H carboxylation of furoate



			Static		Flowing[a]	
$K^+ : Cs^+$	Scale	*T*	$FDCA^{2-}$	Starting material	$FDCA^{2-}$	Starting material
Cs^+ only	1 mmol	265 °C	91%	4%	—	—
Cs^+ only	10 mmol	265 °C	91%	0%	—	—
1 : 1	10 mmol	275 °C	56%	12%	79%	10%
2 : 1	10 mmol	290 °C	22%	0%	78%	0%
3 : 1	10 mmol	290 °C	39%	0%	74%	15%
4 : 1	10 mmol	290 °C	33%	0%	71%	18%
20 : 1	10 mmol	300 °C	10%	69%	56%	26%

All yields were determined by comparison to an internal standard by NMR. [a] The flow rate of CO_2 was 140 ml min^{-1}.

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reaction, FDCA was isolated in 66% yield, which is considerably lower than the 78% $FDCA^{2-}$ yield observed in the 10 mmol scale reaction (Table 1). Large amounts of decomposition products were formed. These results reflect the challenge of maintaining good solid–gas contact as the scale is increased in the fixed-bed reactor. In particular, the solid reactants start as a fine powder, but compact into a large mass over the course of the reaction. This process reduces solid–gas contact, which may impede the removal of water and slow carboxylation, thereby increasing decomposition.

To reduce decomposition and improve the yield, we investigated the effects of using a temperature gradient. A 100 mmol scale reaction was performed with the same CO_2 flow rate using a 2 °C h^{-1} ramp from 265 °C to 285 °C, followed by 24 h at 285 °C. This protocol resulted in nearly complete conversion of furoate and an 86% isolated yield of FDCA. Gratifyingly, when the same temperature ramp was used on a 1 mol scale, FDCA was isolated in 89% yield (139 g). The gradient may improve the reaction by slowing or subtly altering the compaction of the solids, thereby enabling better CO_2 access to the reactants in the centre of the reactor and more effective water removal.

Discussion

Our results demonstrate that furoate carboxylation can be used to synthesize FDCA in high yield on a preparative scale (>100 g) and provide insights for further scale-up. The simplicity of the carboxylation reaction is potentially advantageous for process development. No solvent or catalyst is used, which obviates the burden of recovering and/or replenishing these components. Furthermore, the carboxylation performs well with relatively low-purity CO_2 (99.5%), which avoids costly and energy-intensive purification steps required for high-purity gases. The CO_2 could easily be re-circulated in a large-scale process to maximize CO_2 conversion. One possible concern for scale-up is the use of caesium. In the absence of a co-salt, some Cs^+ is required for efficient carboxylation, and the results here indicate that a $K^+:Cs^+$ ratio of 2 : 1 to 4 : 1 is desirable. Although caesium is more abundant than tin,[31] caesium salts have historically been mined on a small scale because of their low demand.[30] It is important to emphasize that the use of carboxylation for large-scale FDCA synthesis would not consume caesium salts because the cations would be recycled after protonation by using bipolar membrane electrodialysis (Fig. 1). Because of its very high water solubility, Cs^+ can be quantitatively recovered upon FDCA precipitation.[20] Assuming Cs^+ has similar transport properties to Na^+ and K^+ in cation exchange membranes, bipolar membrane electrodialysis would require a modest energy demand of a few kWh per kg FDCA.

The reaction kinetics must be substantially improved in order for carboxylation to be used on much larger scales. Our results suggest that this challenge can be addressed by improving mass transport. For the 100 mmol and 1 mol scale reactions, the salt mixture slowly compacts as the reaction proceeds, which greatly slows the reaction and promotes decomposition. These problems are intrinsic to the use of a fixed bed reactor. Strategies that improve the mixing between CO_2 and the solid reactants, such as fluidization or other modes of agitation,[32] are expected to greatly improve the rates and diminish decomposition products upon further scale up. Such approaches have been used for the carboxylation of solid sodium phenolate in the industrial synthesis of aspirin.[33]

The use of CO_2 for the synthesis of high-volume chemicals and fuels has been a longstanding goal in chemistry.[34,35] Carbonate-promoted C–H carboxylation is distinguished from other chemical approaches to CO_2 utilization because it forms C–C bonds without resorting to expensive, energy intensive reagents. While FDCA has yet to be proven as a viable commodity, it has thus far shown great potential to replace terephthalic acid in high volume (>10^7 ton per year) applications. The carboxylation route described here provides a unique opportunity to use CO_2 and waste biomass for a high-volume chemical synthesis.

Conclusions

We have shown that CO_3^{2-}-promoted C–H carboxylation of furoate using K^+/Cs^+ mixtures is an efficient method for synthesizing FDCA on a preparative scale. Salt mixtures with high $K^+:Cs^+$ ratios retain their bulk solid morphology under the reaction conditions, which facilitates reactions under flowing CO_2. Carboxylation competes with furoate decomposition. Removal of the H_2O by-product suppresses decomposition and improves the yield of FDCA. Using a simple fixed bed reactor, we have demonstrated mole-scale furoate carboxylation using a 2 : 1 $K^+:Cs^+$ blend with 89% isolated yield of FDCA. Further improvement of mass transport is expected to enable similar performance on a larger scale.

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