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Communication

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Continuous-flow Production of Succinic Anhydrides via Catalytic β-Lactone Carbonylation by $Co(CO)_4$⊂Cr-MIL-101

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Supporting Information Placeholder

ABSTRACT: Industrial synthesis of succinic acid relies on hydrocarbon oxidation or biomass fermentation routes that suffer from energy-costly separation processes. Here we demonstrate an alternate route to succinic anhydrides via β-lactone carbonylation by heterogeneous bimetallic ion-pair catalysis in $Co(CO)_4^-$-incorporated Cr-MIL-101 ($Co(CO)_4$⊂Cr-MIL-101, Cr-MIL-101 = $Cr_3O(BDC)_3F$, H_2BDC = 1,4-benzenedicarboxylic acid). Postsynthetically introduced $Co(CO)_4^-$ facilitates CO insertion to β-lactone substrates activated by the Lewis acidic Cr(III) centers of the metal−organic framework (MOF), leading to catalytic carbonylation with activity and selectivity profiles that compare favorably to those reported for homogeneous ion-pair catalysts. Moreover, the heterogeneous nature of the MOF catalyst enables continuous production of succinic anhydride through a packed bed reactor, with room temperature β-propiolactone carbonylation activity of 1,300 $mol_{Anhydride}\cdot mol_{Co}^{-1}$ over 6 h on stream. Simple evaporation of the fully converted product stream yields the desired anhydride as isolated solids, highlighting the unique processing advantages conferred by this first example of heterogeneous β-lactone carbonylation pathway.

As a representative four-carbon diacid, succinic acid is finding increasingly wide use as a precursor to high-value products in polymer,[1] food,[2] agriculture,[3] and pharmaceutical[4] industries. Its production, however, has traditionally depended on the energy-intensive benzene or *n*-butane oxidation pathway that features high operating temperatures,[5] limited yields of ~60% due to side oxidation reactions,[6] and incineration of waste gases owing to difficult separation of unreacted substrates.[7] To address this issue, the United States Department of Energy named succinic acid as the first chemical on its list of twelve "Top Value Added Chemicals From Biomass" and fostered the development of milder fermentative routes to succinic acids.[8] There has since been significant progress in the development of commercial-scale fermentation processes to succinates, giving rise to numerous processes with kilotonne-scale annual capacities.[9] Nonetheless, microbial fermentation processes present their own challenges, namely, undesired metabolic flux to byproducts[10] and costly product separation and purification from the fermentation broth that can account for up to 60−70% of the total production cost.[11]

Heterogeneous β-lactone carbonylation is a process that can potentially circumvent current limitations in hydrocarbon oxidation and microbial fermentation pathways. Due to their inherent ring strain, the four-membered β-lactone cycles undergo selective ring-expanding carbonylation to succinic anhydrides under conditions much milder than those of the hydrocarbon oxidation process.[12] Facile recovery of the carbonylated product from the solid catalyst and solvent avoids energy-intensive separations from the fermentation broth required in fermentative processes. In addition, ready availability of β-lactone substrates from industrially accessible epoxides further underscores the intrinsic advantages of the heterogeneous β-lactone carbonylation strategy.[13]

Herein, we report $Co(CO)_4^-$-incorporated Cr-MIL-101 ($Co(CO)_4$⊂Cr-MIL-101, Cr-MIL-101 = $Cr_3O(BDC)_3F$, H_2BDC = 1,4-benzenedicarboxylic acid) as the first heterogeneous catalyst for the selective ring-expansion carbonylation of β-lactones to succinic anhydrides. Competitive activity and selectivity profiles under mild conditions, along with ease of continuous-flow operation and product separations showcase the unique advantages of $Co(CO)_4$⊂Cr-MIL-101. More importantly, these results stand to illustrate the potential of the heterogeneous β-lactone carbonylation pathway as a viable route to large-scale production of succinic anhydrides.

Our initial discovery of β-lactone carbonylation by $Co(CO)_4$⊂Cr-MIL-101 was guided by mechanistic studies on heterocycle carbonylation by homogeneous $[Lewis\ acid]^+[Co(CO)_4]^-$ ion-pair catalysts. It has been proposed that β-lactone carbonylation by $[Lewis\ acid]^+[Co(CO)_4]^-$ follows a mechanism analogous to that of epoxide carbonylation: (1) substrate activation by $[Lewis\ acid]^+$, (2) ring opening by $Co(CO)_4^-$, (3) CO insertion, and (4) product extrusion (Figure 1A).[14] Based on this mechanistic similarity, we hypothesized that our previously reported $Co(CO)_4$⊂Cr-MIL-101, a metal−organic framework (MOF)-based epoxide carbonylation catalyst featuring Lewis acidic Cr(III) secondary building units ion-paired with postsynthetically exchanged $Co(CO)_4^-$ (Figure 1B), would also be able to carbonylate β-lactones to succinic anhydrides.[15] We reasoned that the structural properties of Cr-MIL-101 found favorable for epoxide carbonylation would also be advantageous for β-lactone carbonylation: high surface area, large pore openings (12 Å and 16 Å) and pore diameters (29 Å and 34 Å) for low diffusional barrier to active sites, and high

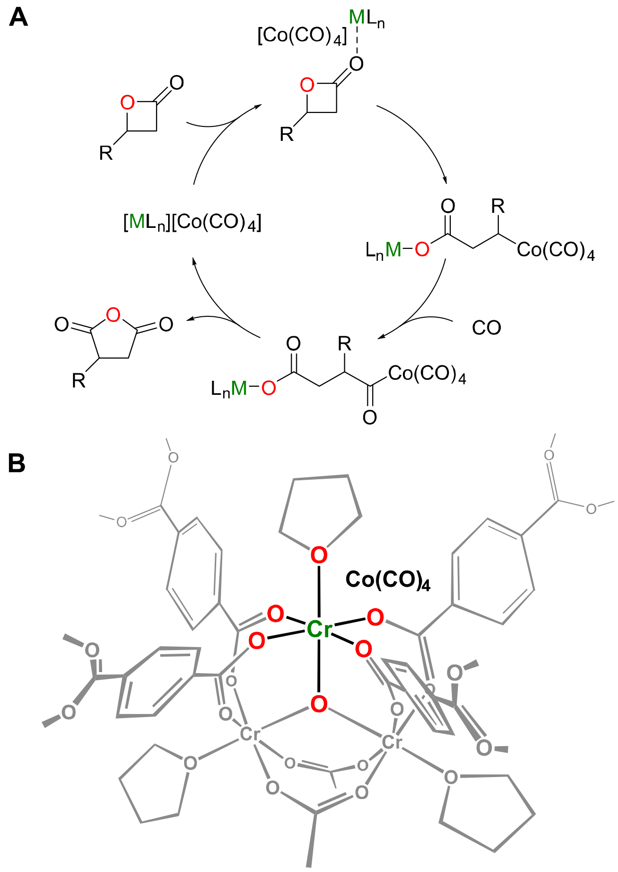


Figure 1. (A) Proposed catalytic cycle for the ring-expansion carbonylation of β-lactones by [Lewis acid]$^+$[Co(CO)$_4$]$^-$.[14] (B) Illustration of the metal cluster structure of Co(CO)$_4$⊂Cr-MIL-101 with coordinated tetrahydrofuran molecules.[15]

chemical and thermal stability for robust catalysis.[16] Synthetic accessibility of the catalyst through relatively inexpensive chromium, cobalt, and terephthalic acid precursors also distinguished Co(CO)$_4$⊂Cr-MIL-101 as an attractive candidate for use in the industrially-relevant β-lactone carbonylation.

Co(CO)$_4$⊂Cr-MIL-101 was prepared as previously reported (Figures S1−S5 and Table S1) and subjected to batch-wise carbonylation reactions with β-butyrolactone as a model substrate. When Co(CO)$_4$⊂Cr-MIL-101 loaded at 0.5 Co mol % with respect to the substrate was exposed to a 1.8 M solution of β-butyrolactone in toluene and 15 bar of CO at 80 °C for 24 h, full conversion of the substrate was observed, in line with what was reported for the homogenous catalyst [(salph)Al(THF)$_2$][Co(CO)$_4$] (salph = *N*,*N*'-*o*-phenylenebis(3,5-di-*tert*-butylsalicylideneimine), THF = tetrahydrofuran).[17] However, the product solution contained not only the desired methylsuccinic anhydride, but also poly(3-hydroxybutyrate) as a major side product (Figure S6). Mixed formation of both the anhydride and the poly(lactone) has been reported for a number of [Lewis acid]$^+$[Co(CO)$_4$]$^-$ catalysts. It is the result of a competitive reaction where subsequent to substrate ring-opening, CO insertion leads to the desired carbonylation cycle while the alternative β-lactone insertion propagates the polymerization reaction (Figure 1A).[14] Given the competitive nature of the two parallel pathways, we sought to increase selectivity to the desired anhydride product by exploiting the differences in the reaction kinetics of the carbonylation and polymerization pathways. To this effect, reaction conditions were altered as follows: (1) substrate concentration was lowered to suppress β-lactone monomer propagation, (2) CO pressure was increased to promote CO insertion, and (3) reaction temperature was lowered to favor carbonylation featuring a presumably lower activation barrier (Figure 2).[14,18] These manipulations combined to promote a clear preference for the carbonylation pathway, with the selectivity for anhydride reaching ~87% under optimized conditions (Figures 2 and S6).

Selective carbonylation activity observed with the β-butyrolactone substrate led us to conduct subsequent studies using β-propiolactone to examine the applicability of Co(CO)$_4$⊂Cr-MIL-101 for the synthesis of the commercially-desirable unsubstituted succinic anhydride. Remarkably, when Co(CO)$_4$⊂Cr-MIL-101 loaded at 0.3 Co mol % with respect to the substrate was charged with a 1.8 M solution of β-propiolactone in toluene and 15 bar of CO for 18 h at room temperature, succinic anhydride was obtained as the sole reaction product in 92% yield without the poly(3-hydroxypropionate) byproduct (Table 1, entry 2 and Figure S7). This corresponds to an overall site time yield of 16 h^{-1}, an improvement over the value of 12 h^{-1} reported for the homogeneous [(salph)Al(THF)$_2$][Co(CO)$_4$] under analogous conditions (Table 1, entry 1).

To probe the catalytic cooperativity between the framework Cr(III) sites and the postsynthetically introduced Co(CO)$_4^-$ in Co(CO)$_4$⊂Cr-MIL-101, Cr-MIL-101 and Na[Co(CO)$_4$] were tested individually for β-propiolactone carbonylation activity (Table 1, entries 3 and 4). Expectedly, both Cr-MIL-101 and Na[Co(CO)$_4$] produced much lower yields, likely due to the absence of Co(CO)$_4^-$ needed for CO insertion and lack of strong Lewis acids needed for substrate activation, respectively. Although using an equimolar mixture of Cr-MIL-101 and Na[Co(CO)$_4$] as a catalyst led to significantly higher yields

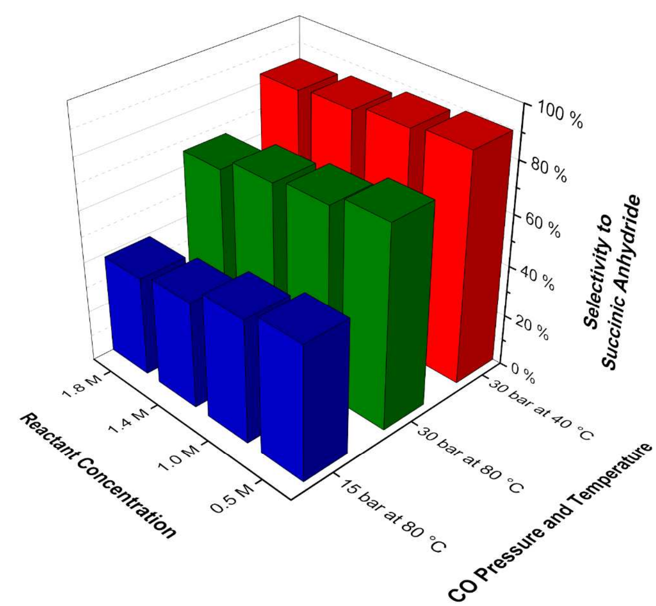
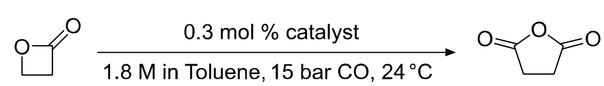


Figure 2. Selectivity to succinic anhydride as a function of the reaction conditions for batch carbonylation of β-butyrolactone by Co(CO)$_4$⊂Cr-MIL-101. Catalyst loaded at 0.5 Co mol % to the substrate in toluene and allowed to react for >75% conversion of the substrate under all conditions tested.

Table 1. Batch Carbonylation of β-Propiolactone.



Entry	Catalyst	*t* (h)	Yield (%)

1	$[(salph)Al(THF)_2][Co(CO)_4]$[17]	24	98
2	$Co(CO)_4$⊂Cr-MIL-101	18	92[a]
3	Cr-MIL-101	18	0[a]
4	$Na[Co(CO)_4]$	18	12[a]
5	Cr-MIL-101 + $Na[Co(CO)_4]$[b]	18	43[a]

[a] As determined by ^{1}H-NMR analysis against mesitylene as a standard. [b] Cr-MIL-101 + $Na[Co(CO)_4]$ = equimolar mixture of the two species.

compared to using either precursor individually, the equimolar mixture was still inferior to $Co(CO)_4$⊂Cr-MIL-101 with pre-installed Cr/Co sites (Table 1, entry 5). We attribute this behavior to an incomplete *in-situ* formation of Cr/Co sites that leads to fractional carbonylation activity for the mixture of Cr-MIL-101 and $Na[Co(CO)_4]$. The need for the coexistence of both the Lewis acidic Cr(III) and $Co(CO)_4^-$ for appreciable carbonylation activity suggests Cr/Co cooperative catalysis to be active for $Co(CO)_4$⊂Cr-MIL-101.

When several solvents were screened for optimizing β-propiolactone carbonylation activity with $Co(CO)_4$⊂Cr-MIL-101, the highest activities were observed with non-coordinating solvents such as toluene and dichloromethane (DCM) (Table S2, entries 1 and 2). Reactions in coordinating solvents greatly reduced carbonylation activity, as exemplified by the low yields from reactions with 1,2-dimethoxyethane, tetrahydrofuran, and acetonitrile (Table S2, entries 3−5). These results deviate from the solvent dependence observed for epoxide carbonylation by $Co(CO)_4$⊂Cr-MIL-101, in which mildly coordinating solvents, such as 1,2-dimethoxyethane, were found to be ideal. A similar discrepancy has been observed for various homogeneous catalysts of the general formula [Lewis acid]$^+$[$Co(CO)_4$]$^-$, where β-lactone carbonylation proceeded much faster in solvents that are less coordinating than those optimal for epoxide carbonylation. This behavior has been accredited to substrate activation and ring-opening being the rate limiting step for β-lactone carbonylation, where Lewis basic solvents more effectively compete for coordination to the Lewis acidic metal sites and hinder substrate ring-opening by $Co(CO)_4^-$ (Figure 1A).[14] Observation of an analogous solvent dependence with $Co(CO)_4$⊂Cr-MIL-101 lends credence that a similar mechanistic explanation may be applicable to β-lactone carbonylation by $Co(CO)_4$⊂Cr-MIL-101.

In order to confirm the heterogeneous nature of catalysis by $Co(CO)_4$⊂Cr-MIL-101, a β-propiolactone carbonylation reaction mixture at ~35% conversion was divided into two aliquots, one of which was filtered (Figure S8). When the filtrate and the unfiltered fraction were allowed to further react, the anhydride yield did not increase for the filtrate whereas the unfiltered portion resumed its carbonylation activity. The crystalline structure of $Co(CO)_4$⊂Cr-MIL-101 was also maintained throughout all carbonylation reactions, as verified by powder X-ray diffraction analysis of spent $Co(CO)_4$⊂Cr-MIL-101 (Figure S9).

Having confirmed the heterogeneous β-lactone carbonylation activity by $Co(CO)_4$⊂Cr-MIL-101, we designed a laboratory-scale packed-bed reactor process to study $Co(CO)_4$⊂Cr-MIL-101 under continuous-flow conditions (Figure S10). As a singular example among all β-lactone carbonylation catalysts developed to date, when $Co(CO)_4$⊂Cr-MIL-101 at room temperature was subjected to a flow of 0.1 M β-propiolactone in DCM at 0.1 ml/min or a weight hourly space velocity (WHSV) of 1,200 h^{-1} and an excess CO flow of 30 ml/min at 45 bar, succinic anhydride was obtained as the sole product at 1,300 $mol_{Anhydride}\cdot mol_{Co}^{-1}$ over 6 h on stream (Figures 3A and S11). $Co(CO)_4$⊂Cr-MIL-101 was also able to carbonylate β-butyrolactone cleanly to the respective methylsuccinic anhydride, with an activity of 360 $mol_{Anhydride}\cdot mol_{Co}^{-1}$ over 60 h on stream at 40 °C when exposed to a flow of 0.5 M β-butyrolactone in toluene at 0.02 ml/min or a WHSV of 7.1 h^{-1} and an excess CO flow of 30 ml/min at 30 bar (Figures 3B and S11). The dramatically higher activity observed with β-propiolactone is in line with the proposed S_N2 attack on the β-carbon of the lactone by $Co(CO)_4^-$ (Figure 1A), where decreased steric hindrance on the β-carbon leads to a significant increase in activity.[14] Carbonylation activity was also highly sensitive to CO pressure, where stability of the observed activity profiles was impaired

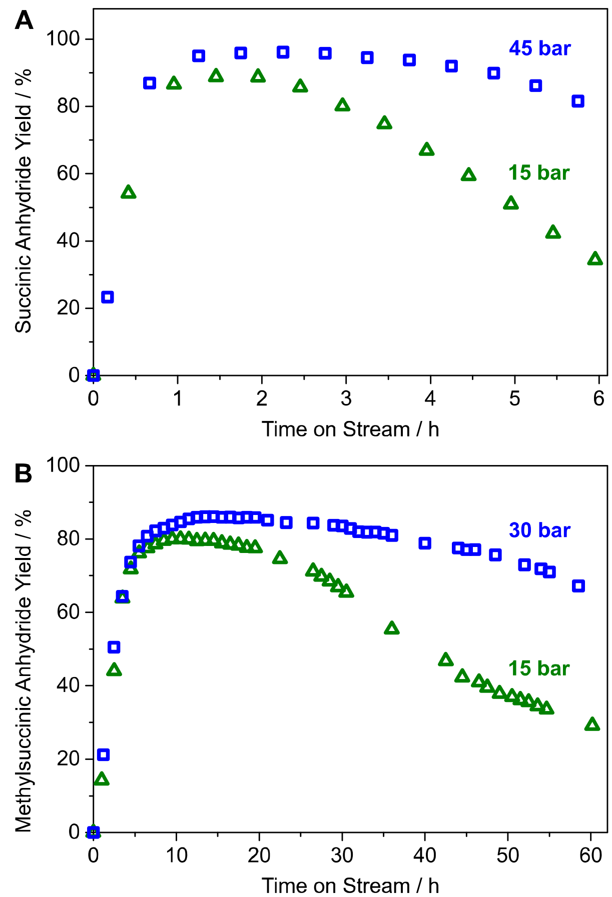


Figure 3. (A) Continuous-flow carbonylation of β-propiolactone by $Co(CO)_4$⊂Cr-MIL-101. Reaction conditions: 0.1 ml/min of 0.1 M β-propiolactone in DCM, 30 ml/min of CO at 45 bar or 15 bar, and 6.0 mg catalyst at 21 °C. (B) Continuous-flow carbonylation of β-butyrolactone by $Co(CO)_4$⊂Cr-MIL-101. Reaction conditions: 0.02 ml/min of 0.5 M β-butyrolactone in toluene, 30 ml/min of CO at 30 bar or 15 bar, and 130 mg catalyst at 40 °C.

at lower CO pressures for both β-propiolactone and β-butyrolactone substrates (Figure 3). This behavior parallels the analogous CO pressure dependence observed in batch carbonylation studies, suggesting that competing side reactions, such as β-lactone homopolymerization, may be a major cause of deactivation.

A key feature of β-lactone carbonylation by $Co(CO)_4$⊂Cr-MIL-101 is the ease of product recovery from the heterogeneous catalyst. When catalyst loading was increased to fully convert the substrate in a continuous-flow β-propiolactone carbonylation, ambient evaporation of the volatile DCM from the product stream led to isolation of the desired succinic anhydride as a crystalline solid (Figure S12). Similar results were obtained from batch-wise β-propiolactone carbonylation studies, where filtration of the solid catalyst and subsequent evaporation of the fully converted product mixture resulted in recovery of succinic anhydride crystals. These simple operations greatly contrast the complicated separations schemes required in hydrocarbon oxidation or microbial fermentation processes (e.g., NH_3/H_2SO_4-assisted succinate precipitation, NaOH-assisted electrodialysis, amine-assisted reactive extraction, etc.[19]) and further corroborates the potential of our heterogeneous β-lactone carbonylation pathway for the industrial production of succinic anhydrides.

In summary, we report $Co(CO)_4$⊂Cr-MIL-101 as the first heterogeneous catalyst for the selective ring-expanding carbonylation of β-lactones to succinic anhydrides. Its facile application to a packed-bed reactor process for continuous production and recovery of succinic anhydrides substantiates the potential efficacy of the heterogeneous β-lactone carbonylation pathway. We ascribe the favorable performance of the catalyst to the intrinsic structural advantages of the MOF platform, which supports precise coordination geometries[20–22] as isolated single sites[23–25] within a robust porous scaffold[26–28] for novel catalytic applications. We believe these unique structural properties could be leveraged for the development of an improved class of heterogeneous catalysts. In addition, identification of an optimum flow reactor configuration through reaction kinetics studies is anticipated to further enhance the performance of the β-lactone carbonylation process.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental information and supplementary data (PDF)

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Notes

The authors are listed as inventors on a patent pertaining to the results herein.

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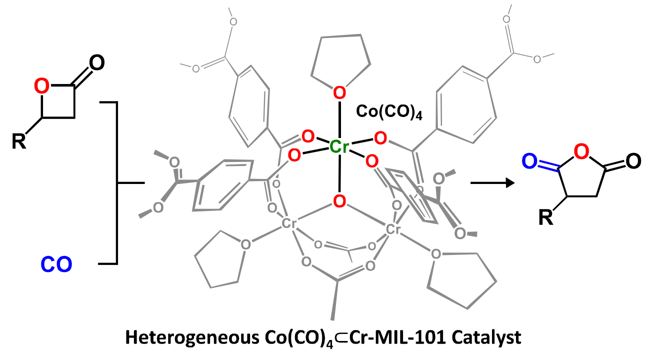

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