Heterogeneous Epoxide Carbonylation by Cooperative Ion-Pair Catalysis in Co(CO)$_4$-Incorporated Cr-MIL-101

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Supporting Information

ABSTRACT: Despite the commercial desirability of epoxide carbonylation to β-lactones, the reliance of this process on homogeneous catalysts makes its industrial application challenging. Here we report the preparation and use of a Co(CO)$_4$-incorporated Cr-MIL-101 (Co(CO)$_4$⊂Cr-MIL-101, Cr-MIL-101 = Cr$_3$O(BDC)$_3$F, H$_2$BDC = 1,4-benzenedicarboxylic acid) heterogeneous catalyst for the ring-expansion carbonylation of epoxides, whose activity, selectivity, and substrate scope are on par with those of the reported homogeneous catalysts. We ascribe the observed performance to the unique cooperativity between the postsynthetically introduced Co(CO)$_4$ and the site-isolated Lewis acidic Cr(III) centers in the metal–organic framework (MOF). The heterogeneous nature of Co(CO)$_4$⊂Cr-MIL-101 allows the first demonstration of gas-phase continuous-flow production of β-lactones from epoxides, attesting to the potential applicability of the heterogeneous epoxide carbonylation strategy.
its metal clusters contain structurally similar octahedral Cr(III) ions that are coordinated equatorially by the oxygen atoms of the bridging terephthalate ligands and axially by a \( \mu_3 \)-oxygen atom and a solvent molecule (Figure 1D).\(^{18}\) Crucially, Cr-MIL-101 has a cationic framework with ion-exchangeable F\(^-\).\(^{19,20}\) We surmised that exchanging F\(^-\) with Co(CO)\(_4\)\(^-\) would lead to the isolation of a heterogeneous catalyst of the general formula \([\text{Lewis acid}]^+\,[\text{Co(CO)}_4]^–\), mimicking that of the homogeneous species. Other innate properties of Cr-MIL-101 that we deemed favorable for catalysis were its high hydrothermal and chemical stability, large surface area (4100 m\(^2\)/g as measured by N\(_2\) adsorption), large windows (12 and 16 Å) and pores (29 and 34 Å) for ready diffusion of reaction species, site-isolation of the Lewis acidic Cr(III) centers for robust catalysis, and facile synthesis using inexpensive chromium and terephthalic acid precursors.\(^{21}\) Similar strategies to leverage the intrinsic stability,\(^{22,23}\) porosity,\(^{24,25}\) and site-isolation\(^{26,28}\) of MOFs have proven to be effective in their applications to heterogeneous catalysis. Therefore, postsynthetic ion exchange of Co(CO)\(_4\)\(^-\) into Cr-MIL-101 was sought for the formation of a heterogeneous \([\text{Lewis acid}]^+\,[\text{Co(CO)}_4]^–\) system.

The charge-balancing F\(^-\) anions in the as-synthesized Cr-MIL-101 are directly coordinated to the Cr(III) sites of the framework.\(^{18}\) To replace these framework-bound anions with uncoordinated Co(CO)\(_4\)\(^-\), anion exchange was performed in two discrete steps: (1) exchange of the bound F\(^-\) with mobile Cl\(^-\) using AlCl\(_3\) and (2) exchange of the mobile Cl\(^-\) with Co(CO)\(_4\)\(^-\) using Na[Co(CO)\(_4\)]. In the initial anion exchange, Al\(^{3+}\) shows greater affinity to F\(^-\) than the framework Cr(III) sites, resulting in the abstraction of F\(^-\) from the MOF.\(^{19}\) The consequent charge imbalance is compensated by the inclusion of Cl\(^-\) into the framework. This sequence of events was tracked by energy dispersive X-ray spectroscopy (EDX) analysis of the Cr-MIL-101 sample before (Cr-MIL-101-F) and after (Cr-MIL-101-Cl) soaking in a solution of AlCl\(_3\) (Figure 2A). In the EDX spectra, the F K\( \alpha \) peak observed at 0.68 keV for Cr-MIL-101-F was replaced by the Cl K\( \alpha \) peak at 2.62 keV for Cr-MIL-101-Cl upon AlCl\(_3\) treatment and extensive washing. The absence of the F K\( \alpha \) and Al K\( \alpha \) peaks in the spectrum of Cr-MIL-101-Cl implies complete exchange of F\(^-\) by Cl\(^-\) and negligible retention of [AlCl\(_3\)F]\(^-\) or any potentially unreacted AlCl\(_3\). The structure of the MOF remained intact after the ion exchange as evidenced by the retention of crystallinity in the powder X-ray diffraction (PXRD) analysis of Cr-MIL-101-Cl (Figure S1).

Subsequent anion exchange between Cr-MIL-101-Cl and Na[Co(CO)\(_4\)] was analyzed by EDX and attenuated total reflectance infrared spectroscopy (ATR-IR), both of which

Figure 1. (A) Proposed catalytic cycle for the ring-expansion carbonylation of epoxides by \([\text{Lewis acid}]^+\,[\text{Co(CO)}_4]^–\).\(^{17}\) (B) Illustration of the structure of \([\text{(OEP)}\text{Cr(THF)}_2]^+\,[\text{Co(CO)}_4]^–\) (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato, THF = tetrahydrofuran).\(^{14}\) (C) Illustration of the structure of \([\text{(salph)}\text{Cr(THF)}_2]^+\,[\text{Co(CO)}_4]^–\) (salph = N,N′-o-phenylenebis(3,5-di-tert-butylsalicylideneimine)).\(^{15}\) (D) Illustration of the metal cluster structure of Co(CO)\(_4\)⊂Cr-MIL-101 with coordinated THF molecules.

Figure 2. (A) EDX spectra of Cr-MIL-101-F, Cr-MIL-101-Cl, and Co(CO)\(_4\)⊂Cr-MIL-101. Au peaks from the preanalysis Au coating of samples. (B) ATR-IR absorption spectra of Cr-MIL-101-Cl and Co(CO)\(_4\)⊂Cr-MIL-101.
confirmed the elimination of Cl⁻ and inclusion of Co(CO)₄⁺ into the framework. Upon soaking Cr-MIL-101-Cl in a Na₂[Co(CO)₄] solution, the Cl Kα peak in the EDX spectrum of the former was replaced by Co Kα and La peaks at 6.92 and 0.78 keV, respectively (Figure 2A). The Co peaks persisted even after repeatedly washing Co(CO)₄Cr-MIL-101 in tetrahydrofuran (THF), which readily solubilizes Na₂[Co(CO)₄], suggesting that Co(CO)₄⁺ is immobilized electrostatically in the MOF through ion-pairing with the Cr(III) Lewis acid sites. The EDX spectrum also evidences the near-absence of the Cl Kα peak at 2.62 keV and the Na Kα peak at 1.04 keV, which are prominent in the spectra of Cr-MIL-101-Cl and Na₂[Co(CO)₄], respectively (Figure S2). These data suggest that the observed Co signal for Co(CO)₄Cr-MIL-101 does not stem from residual Na₂[Co(CO)₄] adsorbed on the surface of the MOF, but rather from substitution of Cl⁻ by Co(CO)₄⁺. The ion exchange and inclusion of Co(CO)₄⁺ in Cr-MIL-101 are further corroborated by the ATR-IR spectrum of Co(CO)₄Cr-MIL-101, which clearly shows the emergence of a single peak at 1888 cm⁻¹ after the exchange procedure (Figure 2B). This band is in line with the characteristic carbonyl stretching mode of the tetrahedral Co(CO)₄⁺ ion in various metal complexes, including those reported for the homogeneous Lewis acid [Co(CO)₄]⁺ epoxide carbylona- lysts. Finally, the structure and porosity of the MOF were retained after this final ion exchange step as evident in the unchanged PXRD pattern for Co(CO)₄Cr-MIL-101 (Figure S1).

The catalytic activity demonstrated by Co(CO)₄Cr-MIL-101 for the ring-expanding carbylonation of epoxides is competitive with that of the homogeneous catalysts. When using neat 1,2-epoxyhexane as a substrate, Co(CO)₄Cr-MIL-101 loaded with 0.5 mol % of cobalt produced the corresponding β-lactone in 86% yield after 5 h under 60 bar of CO at 60 °C (Table 1, entry 6). This corresponds to a calculated site time yield (STY) of 34 h⁻¹, which is comparable to the values reported for a series of homogeneous catalysts under similar reaction conditions (Table 1, entries 1–5).

The solvent dependence of the carbylonaion activity in Co(CO)₄Cr-MIL-101 also mimicked that of the reported homogeneous systems. When a range of solvents was screened for optimizing activity with Co(CO)₄Cr-MIL-101, reactions in weakly coordinating ethers such as 1,2-dimethoxyethane (DME) showed the highest activity. In other solvents, especially more strongly coordinating solvents such as THF, the reactions proceeded at a much slower rate. Identical solvent dependence has been reported for the Cr(III)-based [(salph)-Cr(THF)₃][Co(CO)₄] (salph = N,N'-o-phenylenebis(3,5-di-tert-butylsalicylideneimine)), a homogeneous catalyst that most closely resembles Co(CO)₄Cr-MIL-101 structurally (Figure 1C). Importantly, Co(CO)₄Cr-MIL-101 displays the broad functional group tolerance of the homogeneous catalysts as evidenced by its activity toward an array of aliphatic epoxides as well as glycidyl ether and epichlorohydrin (Table 1, entries 7–10). It is also noteworthy that the observed catalytic activity of Co(CO)₄Cr-MIL-101 is orders of magnitude higher than that of an immobilized homogeneous catalyst under similar reaction conditions.

To validate the heterogeneous nature of the observed catalytic activity, Co(CO)₄Cr-MIL-101 was isolated from a portion of the epoxide carbylonaion reaction mixture by filtration at ~15% conversion (Figure S3). When the acquired filtrate and the unfiltered mixture were both subjected to the standard reaction conditions again, the filtrate did not show any increase in β-lactone yield whereas the unfiltered portion resumed its epoxide carbylonaion activity. The structural integrity of Co(CO)₄Cr-MIL-101 was also retained after all epoxide carbylonaion reactions as confirmed by PXRD analysis of spent Co(CO)₄Cr-MIL-101 (Figure S1).

To verify the catalytic cooperativity between the Cr(III) sites and Co(CO)₄⁺ in Co(CO)₄Cr-MIL-101, Cr-MIL-101-F, Cr-MIL-101-Cl, and Na₂[Co(CO)₄] were tested for epoxide carbylonaion activity (Table S1). All systems displayed negligible product formation when subjected to a 5 h reaction with neat 1,2-epoxyhexane at 0.5 mol % loading, 60 bar CO, and 60 °C. In addition, no substantial catalytic activity was observed when HKUST-1 (Cu₂BTC₂, H₂BTC = benzene-1,3,5-tricarboxylic acid) (Figure S4), a representative Lewis acidic MOF with Cu(II) sites, was subjected to the same reaction conditions.

Table 1. Catalysts for the Ring-Expansion Carbylonaion of Epoxides

| entry | catalyst | R | solvent | P₀ (bar) | T (°C) | t (h) | [epoxide] /[Co]¹ | yield (%) | STY (h⁻¹)b | ref |
|-------|----------|---|---------|---------|--------|------|----------------|-----------|-----------|-----|
| 1     | BF₃Et₂O + [PPN][Co(CO)₄]²⁻ | n-Bu | DME⁻ | 62 | 80 | 24 | 50 | 66 | 1.4 | 10 |
| 2     | [(Cp)₂Ti(THF)₅][Co(CO)₄]¹⁻ | (CH₃)₂HC≡CH₂ | DME⁻ | 62 | 60 | 4 | 20 | 90 | 4.5 | 11 |
| 3     | [(salph)Al(THF)₃][Co(CO)₄]²⁻ | n-Bu | neat | 62 | 60 | 6 | 350 | 40 | 23 | 13 |
| 4     | [(TPP)Cr(THF)₃][Co(CO)₄]²⁻ | n-Bu | neat | 62 | 60 | 6 | 350 | >99 | 58 | 13 |
| 5     | [(OEP)Cr(THF)₃][Co(CO)₄]²⁻ | n-Bu | neat | 62 | 60 | 6 | 4500 | >99 | 740 | 14 |
| 6     | Co(CO)₄Cr-MIL-101 | n-Bu | neat | 60 | 60 | 6 | 200 | 86 | 34 | this work |
| 7     | Co(CO)₄Cr-MIL-101 | n-Bu | neat | 60 | 60 | 1 | 200 | 88 | 180 | this work |
| 8     | Co(CO)₄Cr-MIL-101 | (CH₃)₂HC≡CH₂ | DME⁻ | 60 | 60 | 1.5 | 200 | 93 | 120 | this work |
| 9     | Co(CO)₄Cr-MIL-101 | CH₂OEt | DME⁻ | 60 | 60 | 4 | 200 | 92 | 46 | this work |
| 10    | Co(CO)₄Cr-MIL-101 | CH₂Cl | DME⁻ | 60 | 60 | 6 | 200 | 56 | 28 | this work |

¹[EPoxide]/[Co] = moles of epoxide per mole of cobalt in catalyst. Site time yield = moles of β-lactone produced per mole of cobalt per hour throughout overall reaction time t. ²PPN = bis(triphenylphosphine)iminium. ³Cp = cyclopentadienyl. salph = N,N'-o-phenylenebis(3,5-di-tert-butylsalicylideneimine). ⁴TPP = 5,10,15,20-tetraphenylporphyrin. ⁵OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato. ⁶DME = 1,2-dimethoxyethane. As determined from an inductively coupled plasma mass spectrometry (ICP-MS) derived cobalt content of the catalyst. As determined by ¹H NMR analysis with mesitylene as an internal standard. 32% of the substrate epoxide remained unreacted.
conditions along with an equimolar amount of Na[Co(CO)₄] (Table S1). These results show that the epoxide carbonylation activity is specific to Co(CO)₄-Cr-MIL-101, where the unique combination of Co(CO)₄⁺ and the strong Lewis acidic Cr(III) sites of the Cr-MIL-101 framework is required for cooperative catalysis. We note that an equimolar mixture of the as-synthesized Cr-MIL-101 and Na[Co(CO)₄] also showed β-lactone formation under reaction conditions, presumably due to partial formation of the Cr/Co sites in situ (Table S1). The observed catalytic activity, however, was lower than that of Co(CO)₄-Cr-MIL-101, which exhibits preassembled Cr/CO sites installed within the framework prior to reaction.

Encouraged by the observed heterogeneous epoxide carbonylation activity in liquid-phase batch reactions, we subjected Co(CO)₄-Cr-MIL-101 to a gas-phase continuous-flow reaction using propylene oxide and CO. Uniquely among all known catalysts for this reaction, Co(CO)₄-Cr-MIL-101 showed catalytic epoxide carbonylation activity to form β-butyrolactone under unoptimized reaction conditions: holding Co(CO)₄-Cr-MIL-101 at 70 °C and subjecting it to 20 bar of 0.02 mol% propylene oxide and balance CO flowing at 125 mL/min (at standard temperature and pressure, STP) resulted in STYs of approximately 6 mol%butyrolactone·molCo⁻¹·h⁻¹ and a turnover number of 60 mol%butyrolactone·molCo⁻¹ after 24 h on stream (Figures S5 and S6). Notably, catalytic activity ensued only after in situ removal of the pore-filling THF solvent left over from catalyst synthesis, which presumably blocks substrate access to the Cr/Co active sites. We expect optimization of the reaction conditions to further enhance catalytic performance for a more efficient continuous production of β-lactones. Nonetheless, the ability to perform reactions in the gas phase is a unique feature of our heterogeneous catalyst that is inaccessible to the homogeneous catalysts developed to date.

In summary, we have demonstrated the successful preparation of Co(CO)₄-Cr-MIL-101 and its catalytic activity in the heterogeneous ring-expansion carbonylation of epoxides. We attribute this activity to the cooperativity between the Lewis acidic Cr(III) sites and the postsynthetically incorporated Co(CO)₄⁺. The favorable catalytic performance exemplified by this heterogeneous system and its proof-of-concept application in the first gas-phase continuous production of β-lactones highlight the effectiveness of the heterogeneous epoxide carbonylation pathway and warrant further evaluation of its industrial applicability.

ASSOCIATED CONTENT

Supporting Information
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Experimental information and supplementary data (PDF)

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Notes
The authors declare the following competing financial interest(s): The authors and MIT have filed a patent on some of the results herein.

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