

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

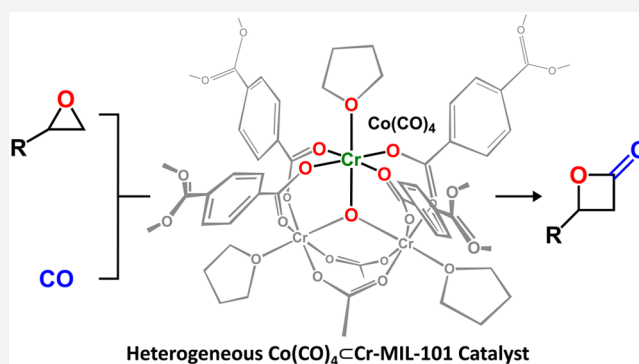
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S Supporting Information

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 $\text{Co}(\text{CO})_4^-$ -incorporated Cr-MIL-101 ($\text{Co}(\text{CO})_4^-$ -Cr-MIL-101, Cr-MIL-101 = $\text{Cr}_3\text{O}(\text{BDC})_3\text{F}$, H_2BDC = 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 $\text{Co}(\text{CO})_4^-$ and the site-isolated Lewis acidic Cr(III) centers in the metal–organic framework (MOF).

The heterogeneous nature of $\text{Co}(\text{CO})_4^-$ -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.



β -Lactones have received considerable attention due to their prevalence as key intermediates in numerous synthetic pathways.^{1,2} Their versatility stems from the inherent ring strain in the four-membered cycles, which renders β -lactones highly susceptible to a rich variety of ring-opening and ring-expanding transformations. The high commercial value of the resulting products, namely, β -hydroxy acids,³ biodegradable polyhydroxyalkanoates,⁴ and succinic anhydrides,⁵ further substantiates the industrial relevance of β -lactone chemistry. Despite their obvious utility, β -lactones have traditionally found comparatively little use industrially because their synthesis is challenging.⁶ One particularly attractive solution to this challenge is the ring-expansion carbonylation of epoxides, which exploits the ready availability of epoxides and CO.^{7–9} This route has become viable recently through the work of Alper et al. and Coates et al., who have demonstrated efficient carbonylation of epoxides by a series of homogeneous catalysts constituted of a Lewis acid and $\text{Co}(\text{CO})_4^-$.^{10–15} This discovery has prompted an ongoing effort in the private sector to commercialize an epoxide carbonylation process, despite the homogeneous nature of the catalyst.¹⁶ At large scale, however, heterogeneous processes are clearly desirable, yet to date there are no competent heterogeneous catalysts for this process that can compete with the homogeneous systems. The development of an effective heterogeneous catalyst would undoubtedly aid the integration of the epoxide carbonylation process to industrial practice.

Herein, we report the synthesis and use of a $\text{Co}(\text{CO})_4^-$ -incorporated Cr-MIL-101 ($\text{Co}(\text{CO})_4^-$ -Cr-MIL-101, Cr-MIL-101 = $\text{Cr}_3\text{O}(\text{BDC})_3\text{F}$, H_2BDC = 1,4-benzenedicarboxylic acid)

as the first heterogeneous catalyst for the carbonylation of epoxides to β -lactones that is competitive with the homogeneous process. The activity and selectivity profiles of $\text{Co}(\text{CO})_4^-$ -Cr-MIL-101 compare favorably with those of the most active homogeneous catalysts for the liquid-phase batch carbonylation of a range of epoxide substrates. Enabled by the heterogeneous nature of our catalyst, we also report the first proof-of-concept demonstration of gas-phase continuous-flow production of β -butyrolactone from propylene oxide and CO.

In designing a heterogeneous epoxide carbonylation catalyst, we focused our attention on the proposed catalytic cycle for the carbonylation of epoxides by $[\text{Lewis acid}]^+[\text{Co}(\text{CO})_4]^-$: (1) epoxide activation by $[\text{Lewis acid}]^+$, (2) attack by $\text{Co}(\text{CO})_4^-$, (3) migratory insertion and uptake of CO, and (4) ring closing and extrusion (Figure 1A).¹⁷ In view of the irreplaceable role of $\text{Co}(\text{CO})_4^-$ in the proposed CO insertion steps, we identified $[\text{Lewis acid}]^+$ as the modifiable component and investigated its structure in various $[\text{Lewis acid}]^+[\text{Co}(\text{CO})_4]^-$ catalysts. One recurring motif found in the homogeneous catalysts was the pseudo-octahedral Cr(III) center, in which the metal ion is coordinated equatorially by the nitrogen or oxygen atoms of a tetradentate macrocyclic ligand and axially by the oxygen atoms of solvent molecules (Figures 1B and 1C).^{14,15} We reasoned that such a coordination environment favors the activation of epoxides for carbonylation and searched for a heterogeneous analogue. The MOF Cr-MIL-101 was a promising candidate as

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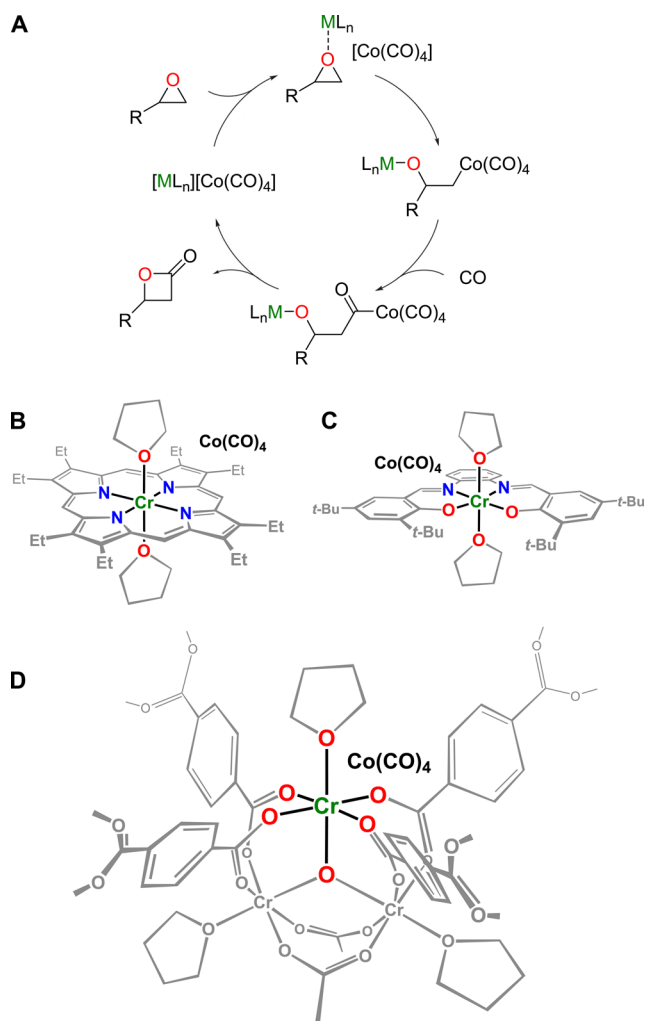


Figure 1. (A) Proposed catalytic cycle for the ring-expansion carbonylation of epoxides by $[\text{Lewis acid}]^+[\text{Co}(\text{CO})_4]^-$.¹⁷ (B) Illustration of the structure of $[(\text{OEP})\text{Cr}(\text{THF})_2]^+[\text{Co}(\text{CO})_4]^-$ (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato, THF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

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 μ_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 $\text{Co}(\text{CO})_4^-$ would lead to the isolation of a heterogeneous catalyst of the general formula $[\text{Lewis acid}]^+[\text{Co}(\text{CO})_4]^-$, 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 ($4100 \text{ m}^2/\text{g}$ 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 $\text{Co}(\text{CO})_4^-$

into Cr-MIL-101 was sought for the formation of a heterogeneous $[\text{Lewis acid}]^+[\text{Co}(\text{CO})_4]^-$ 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 $\text{Co}(\text{CO})_4^-$, 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 $\text{Co}(\text{CO})_4^-$ using $\text{Na}[\text{Co}(\text{CO})_4]$. 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

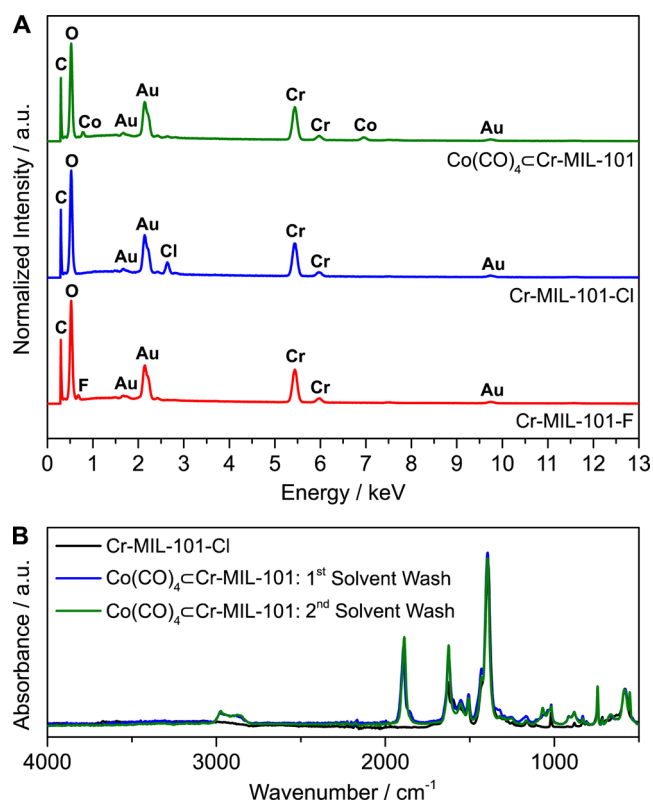
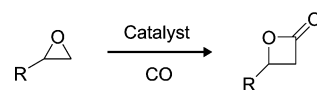


Figure 2. (A) EDX spectra of Cr-MIL-101-F, Cr-MIL-101-Cl, and $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$. Au peaks from the preanalysis Au coating of samples. (B) ATR-IR absorption spectra of Cr-MIL-101-Cl and $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$.

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 $[\text{AlCl}_3\text{F}]^-$ 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 $\text{Na}[\text{Co}(\text{CO})_4]$ was analyzed by EDX and attenuated total reflectance infrared spectroscopy (ATR-IR), both of which

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



entry	catalyst	R	solvent	P_{CO} (bar)	T ($^{\circ}\text{C}$)	t (h)	[epoxide]/ [Co] ^a	yield (%)	STY (h^{-1}) ^b	ref
1	$\text{BF}_3 \cdot \text{Et}_2\text{O} + [\text{PPN}]^+[\text{Co}(\text{CO})_4]^-$	<i>n</i> -Bu	DME ^h	62	80	24	50	66	1.4	10
2	$[(\text{Cp})_2\text{Ti}(\text{THF})_2]^+[\text{Co}(\text{CO})_4]^-$	$(\text{CH}_2)_2\text{HC}=\text{CH}_2$	DME ^h	62	60	4	20	90	4.5	11
3	$[(\text{salph})\text{Al}(\text{THF})_2]^+[\text{Co}(\text{CO})_4]^-$	<i>n</i> -Bu	neat	62	60	6	350	40	23	13
4	$[(\text{TPP})\text{Cr}(\text{THF})_2]^+[\text{Co}(\text{CO})_4]^-$	<i>n</i> -Bu	neat	62	60	6	350	>99	58	13
5	$[(\text{OEP})\text{Cr}(\text{THF})_2]^+[\text{Co}(\text{CO})_4]^-$	<i>n</i> -Bu	neat	62	60	6	4500	>99	740	14
6	$\text{Co}(\text{CO})_4\text{Cr-MIL-101}$	<i>n</i> -Bu	neat	60	60	5	200 ⁱ	86 ^j	34	this work
7	$\text{Co}(\text{CO})_4\text{Cr-MIL-101}$	<i>n</i> -Bu	DME ^h	60	60	1	200 ⁱ	88 ^j	180	this work
8	$\text{Co}(\text{CO})_4\text{Cr-MIL-101}$	$(\text{CH}_2)_2\text{HC}=\text{CH}_2$	DME ^h	60	60	1.5	200 ⁱ	93 ^j	120	this work
9	$\text{Co}(\text{CO})_4\text{Cr-MIL-101}$	CH_2OEt	DME ^h	60	60	4	200 ⁱ	92 ^j	46	this work
10	$\text{Co}(\text{CO})_4\text{Cr-MIL-101}$	CH_2Cl	DME ^h	60	60	4	200 ⁱ	56 ^{j,k}	28	this work

^a[Epoxide]/[Co] = moles of epoxide per mole of cobalt in catalyst. ^bSite time yield = moles of β -lactone produced per mole of cobalt in catalyst per hour throughout overall reaction time t . ^cPPN = bis(triphenylphosphine)iminium. ^dCp = cyclopentadienyl. ^esalph = *N,N'*-*o*-phenylenebis(3,5-di-*tert*-butylsalicylideneimine). ^fTPP = 5,10,15,20-tetraphenylporphyrinato. ^gOEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato. ^hDME = 1,2-dimethoxyethane. ⁱAs determined from an inductively coupled plasma mass spectrometry (ICP-MS) derived cobalt content of the catalyst. ^jAs determined by ¹H NMR analysis with mesitylene as an internal standard. ^k32% of the substrate epoxide remained unreacted.

confirmed the elimination of Cl^- and inclusion of $\text{Co}(\text{CO})_4^-$ into the framework. Upon soaking Cr-MIL-101-Cl in a $\text{Na}[\text{Co}(\text{CO})_4]$ solution, the Cl $K\alpha$ peak in the EDX spectrum of the former was replaced by Co $K\alpha$ and $L\alpha$ peaks at 6.92 and 0.78 keV, respectively (Figure 2A). The Co peaks persisted even after repeatedly washing $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ in tetrahydrofuran (THF), which readily solubilizes $\text{Na}[\text{Co}(\text{CO})_4]$, suggesting that $\text{Co}(\text{CO})_4^-$ is immobilized electrostatically in the MOF through ion-pairing with the Cr(III) Lewis acid sites.²⁹ The EDX spectrum also evidences the near-absence of the Cl $K\alpha$ peak at 2.62 keV and the Na $K\alpha$ peak at 1.04 keV, which are prominent in the spectra of Cr-MIL-101-Cl and $\text{Na}[\text{Co}(\text{CO})_4]$, respectively (Figure S2). These data suggest that the observed Co signal for $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ does not stem from residual $\text{Na}[\text{Co}(\text{CO})_4]$ adsorbed on the surface of the MOF, but rather from substitution of Cl^- by $\text{Co}(\text{CO})_4^-$. The ion exchange and inclusion of $\text{Co}(\text{CO})_4^-$ in Cr-MIL-101 are further corroborated by the ATR-IR spectrum of $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$, 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 $\text{Co}(\text{CO})_4^-$ ion in various metal complexes, including those reported for the homogeneous [Lewis acid]⁺ $[\text{Co}(\text{CO})_4]^-$ epoxide carbonylation catalysts.^{12–15,30,31} Finally, the structure and porosity of the MOF were retained after this final ion exchange step as evident in the unchanged PXRD pattern for $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ (Figure S1).

The catalytic activity demonstrated by $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ for the ring-expanding carbonylation of epoxides is competitive with that of the homogeneous catalysts. When using neat 1,2-epoxyhexane as a substrate, $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ 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 $^{\circ}\text{C}$ (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 carbonylation activity in $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ also mimicked that of the reported

homogeneous systems. When a range of solvents was screened for optimizing activity with $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$, 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 $[(\text{salph})\text{Cr}(\text{THF})_2]^+[\text{Co}(\text{CO})_4]^-$ (salph = *N,N'*-*o*-phenylenebis(3,5-di-*tert*-butylsalicylideneimine)), a homogeneous catalyst that most closely resembles $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ structurally (Figure 1C).¹⁵

Importantly, $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ 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 $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ is orders of magnitude higher than that of an immobilized homogeneous catalyst under similar reaction conditions.³²

To validate the heterogeneous nature of the observed catalytic activity, $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ was isolated from a portion of the epoxide carbonylation reaction mixture by filtration at $\sim 15\%$ 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 carbonylation activity. The structural integrity of $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ was also retained after all epoxide carbonylation reactions as confirmed by PXRD analysis of spent $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ (Figure S1).

To verify the catalytic cooperativity between the Cr(III) sites and $\text{Co}(\text{CO})_4^-$ in $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$, Cr-MIL-101-F, Cr-MIL-101-Cl, and $\text{Na}[\text{Co}(\text{CO})_4]$ were tested for epoxide carbonylation 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 $^{\circ}\text{C}$. In addition, no substantial catalytic activity was observed when HKUST-1 (Cu_3BTC_2 , H_3BTC = benzene-1,3,5-tricarboxylic acid) (Figure S4), a representative Lewis acidic MOF with Cu(II) sites,³³ was subjected to the same reaction

conditions along with an equimolar amount of $\text{Na}[\text{Co}(\text{CO})_4]$ (Table S1). These results show that the epoxide carbonylation activity is specific to $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$, where the unique combination of $\text{Co}(\text{CO})_4^-$ 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 $\text{Na}[\text{Co}(\text{CO})_4]$ 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 $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$, 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 $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ to a gas-phase continuous-flow reaction using propylene oxide and CO. Uniquely among all known catalysts for this reaction, $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ showed catalytic epoxide carbonylation activity to form β -butyrolactone under unoptimized reaction conditions: holding $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ 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 $6 \text{ mol}_{\beta\text{-butyrolactone}} \cdot \text{mol}_{\text{Co}}^{-1} \cdot \text{h}^{-1}$ and a turnover number of $60 \text{ mol}_{\beta\text{-butyrolactone}} \cdot \text{mol}_{\text{Co}}^{-1}$ 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 $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ 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 $\text{Co}(\text{CO})_4^-$. The favorable catalytic performance exemplified by this heterogeneous system and its proof-of-concept application in the first gas-phase continuous production of β -lactone 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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