

# Enhancing the Catalytic Activity in the Solid State: Metal–Organic Frameworks to the Rescue

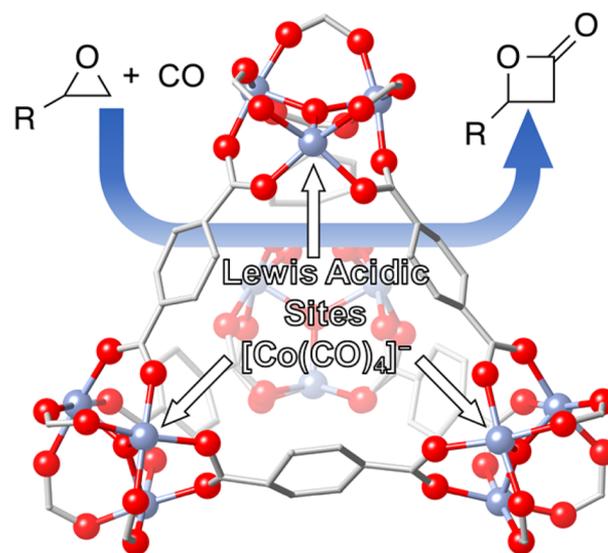
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**Catalytic metal–organic frameworks may hold the key to making more environmentally friendly plastics.**

With a double life as an indispensable consumer commodity but also an environmental scourge, plastics are omnipresent in the modern age, produced at massive scales and a constant source of political and societal debate. Compared to the commonly used polypropylene-based plastics, polyester plastics using poly((R)-β-hydroxybutyrate) (PHB) are biodegradable and therefore have much less of a harmful environmental impact. Widespread use of PHB is, however, limited as the polyester is typically biosynthetically produced from the microorganism *Alcaligenes eutrophus*, resulting in a market cost ~16× greater than that of polypropylene.<sup>1</sup> As an alternative proposed pathway, the ring-opening polymerization of β-lactones offers many promising advantages over the biosynthetic route.<sup>2</sup> Historically, β-lactones have been predominantly synthesized via either a [2 + 2] cycloaddition reaction or cyclization of β-halosalts. Because of low yields, these processes are not compatible with large-scale industrial practices consequently resigning β-lactones as niche reagents for natural product syntheses. However, the seminal works by Apler et al.<sup>3</sup> and later Coates et al.<sup>4</sup> demonstrated that by combining a Lewis acid with a cocatalyst  $\text{Co}(\text{CO})_4^-$  CO could be catalytically inserted into epoxides producing β-lactones. Unfortunately, these systems lacked heterogeneous analogues with similar activities, significantly hindering their industrial use. In this issue of *ACS Central Science*, Park et al. took the lessons learned from these homogeneous systems and rationally designed a metal–organic framework (MOF)-based heterogeneous catalyst to facilitate the production of β-lactones, reinvigorating intrigue for the possible application of industrial-scale production of β-lactones and subsequently polyhydroxybutyrate plastics.<sup>5</sup>



**Figure 1.** An example of a tetrahedral cage in Cr(III)-MIL-101 with ligated solvent and counterions removed for simplicity. Cr: Blue, O: Red, C: Gray.

In this paper, the benefits of using MOFs—porous materials composed of metal nodes connected via organic linkers—as the catalyst platform are at the forefront: structural tunability, high surface area, site-isolation, and periodicity are all highly sought-after attributes for any efficient heterogeneous catalyst.<sup>6</sup> Although amorphous-phase catalysts and/or supports may produce active materials, the challenge of unambiguously characterizing physical properties of the active sites hinders the process of rational design to improve them. Conversely, the crystalline nature of MOFs offers opportunities to use their nodes as structurally characterizable active sites where mechanistic details of a catalytic process may be teased out.<sup>7</sup> Herein, the structure of Cr(III)-MIL-101 (Figure 1) lends itself perfectly as the catalyst support for epoxide carbonylation for two primary reasons: (1) the cationic framework allows for efficient ion-exchange of the  $\text{F}^-$  counterions with the  $\text{Co}(\text{CO})_4^-$

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cocatalyst (the composite material hereafter named  $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$ ), ensuring close proximity of catalyst and activator, and (2) the solvent molecules bound via dative bonds to Cr(III) sites can be removed, generating Lewis acidic Cr(III) sites to activate the epoxide. Notably, even with extensive washing, the  $\text{Co}(\text{CO})_4^-$  species persists in the framework indicating its strong electrostatic interactions with the framework, such that deleterious leaching under catalytic conditions is prevented.

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Upon addition of a catalytic amount of the composite catalyst to 1,2-epoxyhexane with 60 bar CO at 60 °C, the corresponding  $\beta$ -lactone was formed with a site time yield (STY) of  $34 \text{ h}^{-1}$  rendering it the most active heterogeneous  $[\text{Lewis Acid}]^+[\text{Co}(\text{CO})_4]^-$  epoxide carbonylation catalyst reported thus far. Remarkably, given the rich site density within the material, this rate is comparable to that of homogeneous-based systems under similar conditions. Importantly, it also exhibits the same versatility of the homogeneous systems, as evidenced by its wide substrate scope. The catalytic activity is solvent-dependent, where strongly coordinating solvents presumably block the Cr(III) sites thereby inhibiting epoxide activation. These observations are consistent with previously studied homogeneous systems, lending credence that the reactivity of the heterogeneous  $\text{Co}(\text{CO})_4\text{Cr-MIL-101}$  can be predicted due to the uniform identity of its active sites. Aiming to further confirm its merit as a heterogeneous catalyst, continuous-flow gas-phase carbonylation of propylene oxide was tested. After an initial activation period in which coordinated tetrahydrofuran was expelled to open a coordination-site on the Lewis acidic Cr(III),  $\beta$ -butyrolactone was produced, marking the first successful implementation of these catalytic systems in the ring opening-expansion carbonylation of epoxides in the gas-phase.

Taking inspiration from the modification of the Lewis acidic sites in zeolites, it will be intriguing to see the advantages that MOFs can offer in catalyst design.

Facilitated by the modularity of MOFs and the diverse toolbox of postsynthetic modification techniques that they offer,<sup>8</sup> it is conceivable that the catalytic activity and/or stability of these systems may be improved by structural tuning of the active site. Taking inspiration from the modification of the Lewis acidic sites in zeolites,<sup>9</sup> it will be intriguing to see the advantages that MOFs can offer in catalyst design. Given the predominant position zeolites hold in industrial catalytic processes, it is tantalizing to think of the potential roles that MOF-based materials may play with their equally well-defined active sites. As this paper shows, MOFs afford an additional class of support that may push the boundaries in catalytic science. As more and more stable MOFs are being discovered, researchers are just beginning to tap into the potential of this class of material as industrially viable catalysts.

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#### Notes

The authors declare no competing financial interest.

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