

Designing novel multifunctional MOF catalysts for sustainable CO₂ utilization

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A multifunctional catalyst, combining the carbon capture properties of the metal organic framework, Cr-MIL-101, with the catalytic activity of substituted imidazoles organocatalysts has, for the first time, shown excellent activity in CO₂ utilization. Our design strategy purposefully brings the active imidazole in close proximity to the carbon capturing Cr³⁺ metal nodes to create a heterogeneous catalyst that can selectively form cyclic carbonate species in high yield under mild conditions. Through the use of in situ characterization and methodical catalytic testing we generate structure-property correlations to probe the mechanism of this process, with the aim of optimizing our novel catalytic design for CO₂ utilization.

1. Scope

Currently the combustion of fossil fuels is the leading contributor to the global energy supply, resulting in increased levels of CO₂ in the atmosphere, rising from 320 ppm to 405 ppm over the course of the last 60 years. As such, the use of CO₂ as a feedstock is highly desirable. This requires novel catalysts to be designed to activate this comparatively inert molecule, combining a catalytic site tailored for CO₂ transformations with a support that can readily adsorb CO₂.

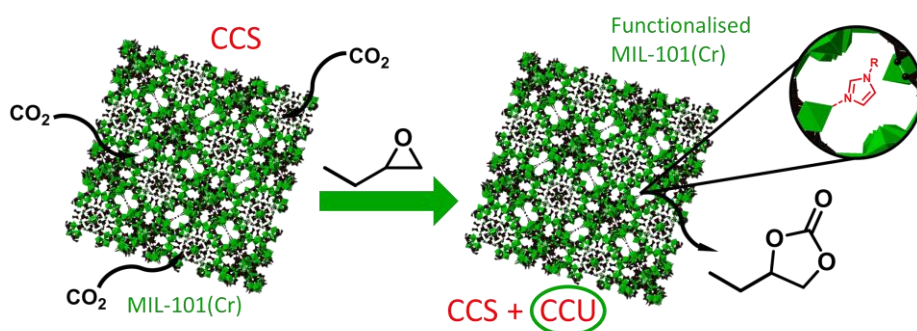


Figure 1: Designing a multifunctional Cr-MIL-101 system for Carbon Utilization.

Metal organic frameworks (MOFs) are regularly used as CO₂ sorbents.¹ The organic nature of the linker molecules, connecting the metal nodes, offers a plethora of post-synthesis modifications, and has also been used to introduce catalytic active sites into these

frameworks. However, often overlooked, the metal nodes in many MOF frameworks are coordinatively unsaturated, allowing them to anchor a range of organic moieties to the framework. Imidazoles have shown promise catalyzing the formation of cyclic carbonates from epoxides with CO₂. Typically this synthesis route employs toxic reagents such as phosgene, liberating HCl. Therefore an alternative route with CO₂ is highly appealing. In this work we design new active sites for CO₂ activation by tethering substituted-imidazole organocatalytic species to the available Cr³⁺ metal nodes of a Cr-MIL-101 metal organic framework (Figure 1),¹ for the first time, to create novel species for carbon capture utilization applications.

2. Results and discussion

Our tailored design strategy of combining a CO₂ sorbent, Cr-MIL-101, with an anchored substituted-imidazole species (Figure 1) results in a highly and selective active multifunctional catalyst.² Such species activate CO₂, to exclusively form the cyclic carbonate in high yields (Figure 2), under solvent-free conditions, and achieve turnover frequencies of over 750 hr⁻¹. We further demonstrate the flexibility of our method by varying the degree of substitution on the imidazole. Ranging from a methyl group to a mesitylene substituent, we maintained high conversions and turnover numbers. These findings demonstrate the synergy between the MOF framework and imidazoles for CO₂ utilization applications. Further, the effect of substrate variation has been explored yielding mechanistic insights into this process. These will be discussed in greater detail at the conference.

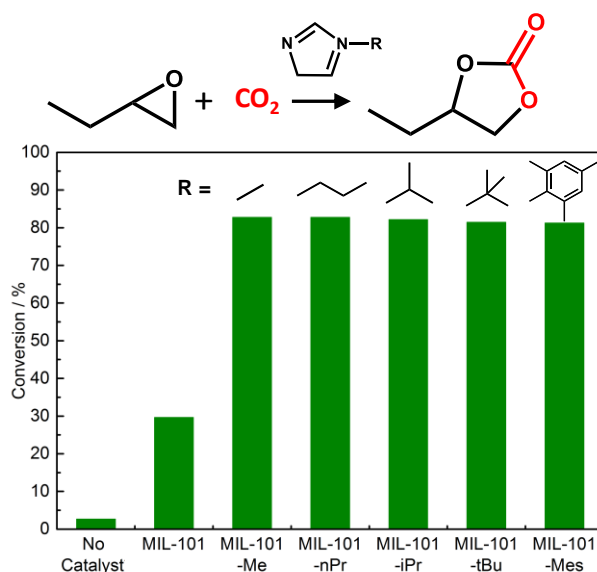


Figure 2: Catalytic results of the imidazole substituted Cr-MIL-101. TOF of over 750 hr⁻¹ are achieved with just CO₂, epoxide and catalyst.

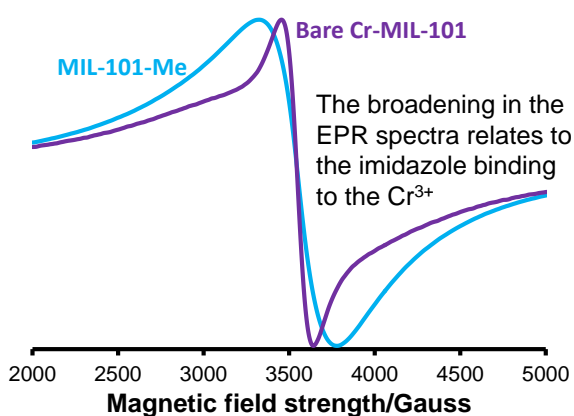


Figure 3: EPR spectra showing the distortion on binding imidazole to Cr-MIL-101.

Through a range of characterization techniques, we show that the structural and compositional integrity of the Cr-MIL-101 has been preserved on functionalizing the imidazoles. Through a range of spectroscopic techniques, we show the binding of the imidazoles to the Cr³⁺ metal nodes (Figure 3). This can be seen through our EPR study, where the distortion of the Cr³⁺ on binding to the imidazole (Figure 3) shows the CO₂ binding site is close to the active imidazole. This has a synergistic effect, improving catalytic performance.^{1,2} We believe the combination of MOF support and organocatalyst allows many possibilities to generate new multifunctional catalysts for CO₂ utilisation.²

3. Conclusions

We have validated our design procedure, combining a known CO₂ sorbent, with an active imidazole species to create a unique tailored multifunctional catalyst for CO₂ utilization. This species achieves high activity and selectivity for the formation of cyclic carbonates and offers a sustainable alternative to traditional synthesis methods. Through the use of a range of characterization techniques we confirm the Cr³⁺ metal nodes of the Cr-MIL-101 support are modified by the imidazole, confirming their close proximity. This work represents a unique design strategy for CO₂ utilization, while offering exciting possibilities for further work in characterization, computational modelling and post-synthesis modification.

References

1. D. Y. Hong, Y. K. Hwang, C. Serre, G. Férey and J. S. Chang, *Adv. Funct. Mater.* **2009**, *19*, 1537–1552.
2. R. Raja, M. E. Potter and S. H. Newland, *Chem. Commun.* **2014**, *50*, 5940-5957.