

Designing Metal Organic Frameworks for Sustainable CO₂ Utilization

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Abstract : Rising CO₂ levels in the atmosphere means that CO₂ is a highly desirable feedstock. This requires specific catalysts to be designed to activate this inert molecule, combining a catalytic site tailored for CO₂ transformations with a support that can readily adsorb CO₂. Metal organic frameworks (MOFs) are regularly used as CO₂ sorbents. The organic nature of the linker molecules, connecting the metal nodes, offers many post-synthesis modifications to introduce catalytic active sites into the frameworks. However, the metal nodes may be coordinatively unsaturated, allowing them to bind to organic moieties. 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 active sites for CO₂ activation, by tethering substituted-imidazole organocatalytic species to the available Cr³⁺ metal nodes of a Cr-MIL-101 MOF, for the first time, to create a tailored species for carbon capture utilization applications. Our tailored design strategy combining a CO₂ sorbent, Cr-MIL-101, with an anchored imidazole results in a highly active and selective multifunctional catalyst, achieving turnover frequencies of over 750 hr⁻¹. 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. Through characterization, we show that the structural and compositional integrity of the Cr-MIL-101 has been preserved on functionalizing the imidazoles. Further, we show the binding of the imidazoles to the Cr³⁺ metal nodes. This can be seen through our EPR study, where the distortion of the Cr³⁺ on binding to the imidazole shows the CO₂ binding site is close to the active imidazole. This has a synergistic effect, improving catalytic performance. We believe the combination of MOF support and organocatalyst allows many possibilities to generate new multifunctional catalysts for CO₂ utilisation. In conclusion, 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. 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.

Keywords : carbonate, catalysis, MOF, utilisation

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