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Designing Metal Organic Frameworks for Sustainable CO_2 Utilization

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Abstract : Rising CO_2 levels in the atmosphere means that CO_2 is a highly desirable feedstock. This requires specific catalysts to be designed to activate this inert molecule, combining a catalytic site tailored for CO_2 transformations with a support that can readily adsorb CO_2. Metal organic frameworks (MOFs) are regularly used as CO_2 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 CO_2. Typically, this synthesis route employs toxic reagents such as phosgene, liberating HCl. Therefore an alternative route with CO_2 is highly appealing. In this work we design active sites for CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2 utilisation. In conclusion, we have validated our design procedure, combining a known CO_2 sorbent, with an active imidazole species to create a unique tailored multifunctional catalyst for CO_2 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 CO_2 utilization while offering exciting possibilities for further work in characterization, computational modelling, and post-synthesis modification.

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