Heterogeneous Zeotype Catalysts for the Direct Utilisation of CO₂

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Due to the increasing levels of carbon dioxide (CO₂) in the atmosphere, there is a growing demand for carbon utilisation technologies. Mono- and polycarbonate materials, synthesised via the catalytic conversion of CO₂ within the pores of high surface area materials, are providing opportunities for the sustainable development of carbon capture and utilisation (CCU) technologies. At this conference, we will present our most recent design strategies which utilise single-site organo-catalysts inside the pores of a zeotype framework for the formation of cyclic carbonates from CO₂ and epoxides. (Figure 1).

Due to the coordinatively unsaturated chromium nodes and large surface area, metal organic framework (MOF) MIL-101(Cr) has been identified as a suitable host for anchoring imidazole-based organo-catalysts. A series of substituted imidazoles were synthesized and coordinated to the MOF at the chromium sites via the unsubstituted N-atom. The series was chosen to provide increasing steric demand in the imidazole side group. Characterisation of the catalyst was conducted by electron paramagnetic resonance (EPR) spectroscopy to probe the Cr³⁺ sites. EPR Spectra for bare MIL-101(Cr) matched the literature well and on binding of the imidazole to the Cr³⁺ sites, broadening of the resonance signals is observed. Further analysis will be conducted by x-ray absorption spectroscopy (XAS) and fourier transform infrared spectroscopy (FT-IR).

For the reaction of 1,2-epoxybutane with CO₂, high activities were observed for all catalysts, achieving 80% conversion with 99% selectivity in 90 minutes. Complete conversion of the epoxide was reached after 6 hours. It is evident that when the imidazoles are heterogenised within the MIL-101 structure, the catalytic ability is greatly enhanced, with a highest turnover frequency (TOF) of 750 hr⁻¹ achieved.

Imidazole grafted MIL-101(Cr) has been shown to be a promising catalyst for the transformation of CO₂ to cyclic carbonates. Combining the absorptive, high surface area properties of MOFs with a targeted organic moiety, we have demonstrated the ability to produce a stable heterogeneous catalyst capable of high catalytic turnovers for CO₂ utilisation.

References