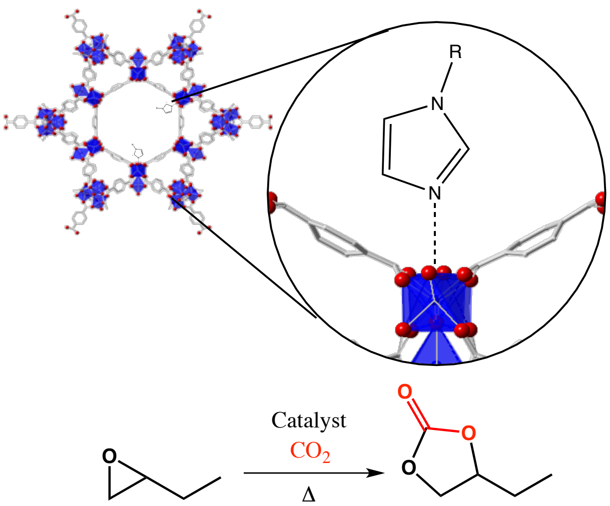
Heterogeneous Zeotype Catalysts for the Direct Utilisation of CO_2

D. J. Stewart[1*], **W. R. Webb[2]**, **M. E. Potter[1]**, **P. J. A. Sazio[1]**, **R. Raja[3**]**

[1]University of Southampton, UK, [2]Institute of Materials Research and Engineering, Singapore
*D.J.Stewart@soton.ac.uk, **R.Raja@soton.ac.uk

Due to the increasing levels of carbon dioxide (CO_2) in the atmosphere, there is a growing demand for carbon utilisation technologies. Mono- and polycarbonate materials, synthesised via the catalytic conversion of CO_2 within the pores of high surface area materials, are providing opportunities for the sustainable development of carbon capture and utilisation (CCU) technologies.[1] 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 CO_2 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.[2] 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 Cr^{3+} sites. EPR Spectra for bare MIL-101(Cr) matched the literature well and on binding of the imidazole to the Cr^{3+} sites, broadening of the resonance signals is observed.[3] Further analysis will be conducted by x-ray absorption spectroscopy (XAS) and fourier transform infrared spectroscopy (FT-IR).



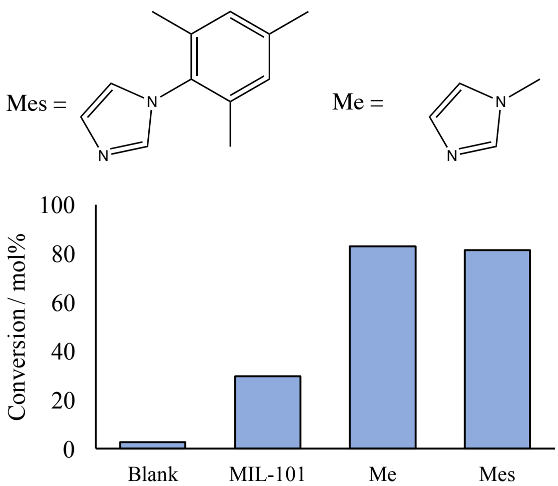


Figure 1 (left): Illustrative representation of imidazole based organo-catalyst bound to vacant Cr^{3+} sites
Figure 2 (right): Conversion (mol%) comparison between unbound MIL-101(Cr) and MIL-101(Cr) grafted with 1-methyl-1H-imidazole and 1-mesityl-1H-imidazole.

For the reaction of 1,2-epoxybutane with CO_2, 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 CO_2 to cyclic carbonates. Combing 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 CO_2 utilisation.

References

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