Improving the CO_2 capture and conversion potential of MOF UiO-66 through sustainable creation of defects

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The daily release of high levels of carbon dioxide (CO_2) into the atmosphere is a serious threat for the sustainable future of the Earth, contributing to catastrophic climate changes. The capture of CO_2 and, subsequent, its conversion into added-value chemicals, is a valuable and cost-effective solution for the reduction of the CO_2 levels. However, bifunctional materials that can conciliate CO_2 capture and conversion simultaneously under sustainable conditions are scarce and needed.[1, 2] Metal-organic frameworks (MOFs) are highly crystalline and porous structures formed by metallic center interconnected with organic ligands. A great number of MOFs have shown promising results in either CO_2 capture or conversion, for example, the cycloaddition of CO_2 with epoxides into cyclic carbonates.[2, 3] Defect engineering, i.e. the deliberate formation of defects in MOFs structures increases the number of active sites, enhancing catalytic efficiency. UiO-66 is a strong candidate for defect induction, since its framework has high structural integrity even containing uncoordinated centers.[3, 4]

In this work, we successfully synthesized a series of defective UiO-66-based materials to enhance the catalytic activity of the parent UiO-66, which were then tested for their ability to capture CO_2. The defects and improved catalytic potential were achieved through a mixed-ligand strategy, based on the mixture of different BDC-based ligands to introduce amine and halogen groups, that theoretically facilitate the opening of the epoxide rings. The materials were synthesized via conventional (solvothermal) and microwave-assisted methods, with the latter demonstrating a significantly lower environmental impact, as confirmed by an LCA study. Characterization techniques such as FTIR, PXRD, SEM-EDS, N_2 sorption, NMR and TGA were employed to confirm the engineered defects. Preliminary catalytic studies to evaluate the MOF performance in the cycloaddition of epichlorohydrin with CO_2 were also performed. This approach envisioned the enhancement of the catalytic performance of UiO-66 in the cycloaddition of CO_2 with epoxides to produce cyclic carbonates, without significant loss of CO_2 adsorption-desorption abilities and through a “greener” synthetic process.

Funding

This work received financial support received from the PT national funds (FCT/MECI, Fundação para a Ciência e Tecnologia / Ministério da Educação, Ciência e Inovação) through the project UID/50006 - Laboratório Associado para a Química Verde - Tecnologias e Processos Limpos.

Acknowledgements

L.C.S. and S.S.B. also thank FCT/MCTES for supporting their contract positions via the Individual Call to Scientific Employment Stimulus (Ref. CEECIND/00793/2018 and Ref. CEECIND/03877/2018, respectively). The position held by I.S.-V. (Ref. 197_97_ARH-2018) was supported by national funds (OE), through FCT, I. P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of article 23 of the Decree-Law 57/2016 of 29 August, changed by Law 57/2017 of 19 July. Simone C. Fernandes was supported by the MPP2030-FCT PhD Grant financed by the Portuguese Foundation for Science and Technology (FCT), under MIT Portugal Program.

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