Amine-functionalized frameworks as highly active catalysts for chemical fixation of CO₂ under solvent and co-catalyst free conditions

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Abstract

Herein, we report the adoption of adjustable composition nitrogen-rich units via introduction of diverse amine groups to an unsaturated metal organic framework, MIL-100(Cr), and the application of the products obtained as novel catalysts in the aspect of CO₂ cycloaddition reactions to afford cyclic carbonates in the absence of cocatalyst and solvent under mild conditions (60 °C, 1 MPa). Incorporation of amine groups to the frameworks leads to substantial increment in the catalytic performance of the structures. The concomitant presence of acidic and basic sites in the structure causes great conversion and selectivity in cycloaddition reactions even for large and bulky epoxides. The comparison of various groups of amines (2-aminopyridine, 1,2-phenylene diamine, 3-aminopyridine and ethylene diamine) incorporated on the surface with different orientations demonstrates the effect of the orientation type in catalytic activity. CO₂ gas sorption measurement helps to better understand the process of catalytic activity. The pristine MOF is unable to progress the reaction without addition of co-catalyst.

Keywords: Metal organic framework, Post-synthetic modification, Co-catalyst free, Superior catalyst, CO₂ cycloaddition

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