



Feature Article

Aqueous microwave-assisted synthesis of non-interpenetrated metal-organic framework for room temperature cycloaddition of CO₂ and epoxides

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ABSTRACT

A multilinker non-interpenetrated metal-organic framework, UMCM-15, was synthesized by using microwave power as an alternative energy-efficient tool for the first time. The synergistic catalytic activity, when combined with a co-catalyst containing a strongly nucleophilic anion, was studied in the solventless room temperature cycloaddition between epoxides and CO₂. Unlike previous reports on UMCM-15 synthesized in the high-boiling solvent dimethylformamide, low boiling water/ethanol mixture was used as the solvent herein. This approach holds potential as a sustainable green methodology. Crystal formation during the microwave-assisted (MW) synthesis was monitored at certain time intervals. The favorable role of non-interpenetrated pillared structures in promoting room temperature CO₂-epoxide cycloaddition reactions was explained by comparing the catalytic efficiency of the three-linker extended pillar-layered non-interpenetrated UMCM-15 with its analogous pillared structures built from two- and three-fold interpenetrated ([Zn₂(BDC)₂(4,4'-bipy)] and [Zn₂(NDC)₂(4,4'-bipy)]) catalytic systems with a single dicarboxylate linker. The efficacy of the microwave-assisted UMCM-15(M) catalyst in cycloaddition reactions was proved by comparing the catalytic activity of UMCM-15(M) with that of the congener made by solvothermal synthesis, UMCM-15(S). In addition, a plausible mechanism for the synergistic operation of the Lewis acid sites and nucleophiles was suggested.

1. Introduction

Over the past few years, extensive research has been conducted on catalysis for developing chemical technologies for the valorization of renewable carbon sources. Carbon dioxide (CO₂) is a widely recognized renewable C1 feedstock for the synthesis of value-added commodity chemicals in an environmentally sustainable way as it is abundant and safe [1–4]. In the case of chemical reactions, the term sustainability encompasses a panorama of perspectives, involving ensuring the implementation of certain green chemistry principles such as the use of green solvents, production of non-toxic wastes, reproducibility, easier purification processes, and the use of inexpensive, abundant, and nonflammable raw materials [5–7]. CO₂-epoxide cycloaddition thus represents a green route for generation of five-membered cyclic carbonates as this method avoids the use of conventional toxic raw materials such as COCl₂ and CO, while availing 100% atom economy

[8–17]. Even though CO₂ meets the requirements of a promising C1 feedstock, to achieve successful CO₂-epoxide cycloaddition, the chemical inertness of CO₂ has to be overcome by developing novel catalytic and technological approaches [18–23]. To add an even greener tag to this strategy for synthesis of cyclic carbonates, it is imperative to critically analyze the characteristics of the catalysts chosen for CO₂-epoxide transformation. Lower energy requirements, the cost of synthesis, chemical-thermal stability, reusability, air and water insensitiveness, etc., are considered important factors.

Metal organic frameworks (MOFs) offer a promising platform for addressing the dual challenge of CO₂ capture and transformation owing to the designable and tunable structures of MOFs and their tailorable surface environment and high internal surface area that can expedite selective CO₂ binding. Moreover, the easily accessible and uniformly distributed high-density active sites throughout the framework and the particle size tunability and porous structures facilitate the transfer of

Abbreviations: CO₂, carbon dioxide; MOF, metal-organic framework; H₂-BDC, benzene-1,4-dicarboxylic acid; 2,6-NDC, 2,6-naphthalenedicarboxylic acid; 4,4'-bipy, 4,4'-bipyridine; PO, propylene oxide; PC, propylene carbonate; SO, styrene oxide; TBAB, tetrabutylammonium bromide

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