Closing the Loop in the Carbon Cycle: Enzymatic Reactions Housed in Metal-Organic Frameworks for CO2 Conversion to Methanol

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Abstract

The preparation of value-added chemicals from carbon dioxide (CO2) can act as a way of reducing the greenhouse gas from the atmosphere. Industrially significant C1 chemicals like methanol (CH3OH), formic acid (HCOOH), and formaldehyde (HCHO) can be formed from CO2. One sustainable way of achieving this is by connecting the reactions catalyzed by the enzymes formate dehydrogenase (FDH), formaldehyde dehydrogenase (FALDH), and alcohol dehydrogenase (ADH) into a single cascade reaction where CO2 is hydrogenated to CH3OH. For this to be adaptable for industrial use, the enzymes should be immobilized in materials that are extraordinarily protective of the enzymes, inexpensive, stable, and of ultra-large surface area. Metal–organic frameworks (MOFs) meet these criteria and are expected to usher in the much-awaited dispensation of industrial biocatalysis. Unfortunately, little is known about the molecular behaviour of MOF-immobilized FDH, FALDH, and ADH. It is also yet not known which MOFs are most promising for industrial enzyme-immobilization since the field of reticular chemistry is growing exponentially with millions of hypothetical and synthesized MOF structures reported at present. This review initially discusses the properties of the key enzymes required for CO2 hydrogenation to methanol including available cofactor regeneration strategies. Later, the characterization techniques of enzyme-MOF composites and the successes or lack thereof of enzyme-MOF-mediated CO2 conversion to CH3OH and intermediate products are discussed. We also discuss reported multi-enzyme-MOF systems for CO2 conversion cognizant of the fact that at present, these systems are the only chance of housing cascade-type biochemical reactions where strict substrate channelling and operational conditions are required. Finally, we delve into future perspectives.