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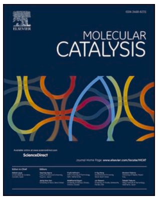

Copper(I)-modified covalent organic framework for CO_2 insertion to terminal alkynes

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ABSTRACT

The carboxylation of terminal alkynes with CO_2 is an attractive route for CO_2 fixation and conversion, and various homogeneous Cu(I) catalysts have been explored for the reaction. However, it is still a challenge to develop efficient heterogeneous catalysts for the conversion under mild conditions. Considering that covalent organic frameworks (COFs) are emerging as versatile platforms for the design of functional materials, we developed a TpBpy-supported Cu(I) catalyst, where TpBpy is a stable imine-type porous COF furnished with rich *N,N*- and N,O-chelating sites for Cu(I) immobilization. The hybrid material can efficiently catalyze the conversion of CO_2 and terminal alkynes to propiolic acids under relatively mild conditions (1 atm CO_2, 60 ℃). The catalytic activity arises from the synergy between the organic framework of TpBpy and the Cu(I) sites. Not merely serving as a porous support to afford isolated and accessible Cu(I) sites, the organic framework itself has its own catalytic activity through the polar and basic N and O functional sites, which could activate the C–H bond and facilitate CO_2 absorption. In addition, the framework also serves as a giant ligand to shift the reversible Cu(I)-catalyzed process in favor of carboxylation. The catalyst shows somewhat reduced activity after reused for three cycles owing to the oxidation of Cu(I) to Cu(II), but it can be easily regenerated by treating with KI.

1. Introduction

Carbon dioxide (CO_2) has long blamed as the main cause of global warming with the industrialization [1,2], and it has also been deemed as a cheap, non-toxic, abundant, and renewable C1 source for synthesis of high value-added chemicals and fuels [3,4]. Among various methodologies for chemical fixation and conversion of CO_2, direct C–H carboxylation of terminal alkynes with CO_2 has attracted increasing attention in recent years. The reaction represents a straightforward approach toward propiolic acids, which are important intermediates for synthesis of fine chemicals, pharmaceuticals and functional polymers [5–7]. Compared to conventional approaches toward propiolic acids (oxidation of propargylic alcohols or propiolaldehydes [8], hydrolysis of corresponding esters [9], and carboxylation of moist-/air-senstive metal-alkylides [10]), direct carboxylation of terminal alkynes not only provides a promising route for conversion and utilization of CO_2 but also has some other advantages such as high atom economy, saving of pre-functionalization steps, and potential compatibility with various functional groups. However, due to the high stability of CO_2, the reaction is actually thermodynamically unfavorable [11]. The situation can be reversed in the presence of a base (e.g., Cs_2CO_3), but the reaction still suffers from the sluggish kinetics. Therefore, many efforts have been devoted to catalytic reactions under milder conditions. The efficient homogeneous catalysts thus far reported are mainly Cu(I) [12] and Ag(I) [13] species (complexes with N-chelates [14] or N-heterocyclic carbenes [15], and simple Ag(I) salts [16]), with sparse other examples. However, homogeneous catalysts complicate product separation and purification, and they are often difficult or unable to be reused, which reduces the total atom economy. Therefore, increasing attention is being paid to the development of heterogeneous catalysts for the reaction. While the studies are overwhelmingly focused on silver nanoparticles composited with various solid supports, such as organic polymers [7,17,18] and metal-organic frameworks (MOFs) [5,19,20], very few heterogeneous catalysts using the cheaper copper have been reported, including MIL-101-supported Pd–Cu nano-alloy [21], ZnO-supported CuBr [22], and Cu(I)-doped carbon nitride-based single-atom catalysts [23]. However, these catalytic systems are still not satisfactory in some aspects such as the use of precious metal, the decaying activity in recycling, and

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