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Ionic liquid-assisted catalytic oxidation of anethole by copper- and iron-based metal-organic frameworks

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ABSTRACT

A synergistic strategy involving ionic liquid (IL) and Cu- or Fe-based metal-organic frameworks (MOFs) has been developed for the selective oxidation of anethole with H_2O_2 and *tert*-butyl hydroperoxide (TBHP). Under the optimum conditions, 74.8%–91.5% conversion of substrate and 92.1%–94.6% selectivity for anisaldehyde were obtained over **Cu-BTC-1** (**BTC**: benzene-1,3,5-tricarboxylate) with the aid of 5.0 mol% [C_{12}mim]Cl using aqueous H_2O_2 as the oxygen source. In contrast, **Fe(PMA)** (**PMA**: pyromellitate) nanorods provided up to 84.0% yield of 4-methoxyphenylacetone in the presence of 5.0 mol% [C_4mim][Cys] by using TBHP oxidant. Notably, amphiphilic [C_{12}mim]Cl and multifunctional [C_4mim][Cys] are favorable for the improved reactivity and good reusability of **Cu-BTC-1** or **Fe(PMA)** owing to the synergistic effects of **Cu-BTC-1**/[C_{12}mim]Cl or **Fe(PMA)**/[C_4mim][Cys] nano/submicro-structures fabricated *in-situ*. In particular, nanoscale stacking of [C_4mim][Cys] on **Fe(PMA)** can be directly demonstrated by TEM. In-depth understanding of the reaction mechanism can be achieved using XRD, FT-IR, DRUV-vis and UV–vis techniques.

1. Introduction

Transformation of biomass and derivatives thereof into chemicals has been paid more attention due to the decline in available fossil resources [1,2]. Anethole is the major component of essential oils extracted from star anise, anise seed or sweet fennel and thus is an alluring feedstock for the production of valuable compounds [2–4]. Among them, anisaldehyde and 4-methoxyphenylacetone are important flavors and intermediates for synthesizing fragrances, pharmaceuticals and agrochemicals [3–7]. Efficient conversion of anethole into anisaldehyde or 4-methoxyphenylacetone has been investigated via vanadium and copper complexes employing H_2O_2 as the green oxidant [3,4,8]. Additionally, anethole cleavage to anisaldehyde was also explored by photochemical and enzyme-mediated methods [9,10]. However, the development of novel heterogeneous catalyst for convenient and highly selective transformation of anethole with H_2O_2 or TBHP is still quite desirable [11].

MOFs have emerged as a promising platform for heterogeneous catalysis owing to ultrahigh porosity, tunable pore size or morphology, and facile modification [12,13]. Since the pioneer work performed by Chui et al. using $[Cu_3(BTC)_2(H_2O)_3]_n$ [14], Cu-MOFs have attracted increasing attention and numerous Cu-containing MOFs, e.g., microporous $[Cu_2^{II,II}(OOCC_6H_{10}COO)_2]\cdot H_2O$ [15], crystalline or amorphized $Cu_3(BTC)_2$ [16], porphyrin@MOF type catalyst CuTNPP@MOF [17], $[Cu(bpy)(H_2O)_2(BF_4)_2(bpy)]$ [18], mixed-node Ag-Cu-BTC [19] and $[\{Cu(L1)(DMF)\}\cdot DMF\bullet H_2O]_n$ derived from pyridyl-based isophthalic acid [20], have been examined in heterogeneous oxidations. Also of considerable interest, iron is intriguing for the design of novel Fe-MOF catalysts because of its advantages such as cheapness, nontoxicity and potential to readily form reactive species (e.g., HO•) [21]. Recently, a variety of Fe-containing MOFs have been reported for heterogeneous catalytic transformations [22–26]. Nonetheless, new approach for anethole oxidation over Cu- or Fe-MOF is relatively unexplored.

The design of novel and simple MOF-based catalytic system with higher stability and activity remains a challenge [27,28]. Mean-

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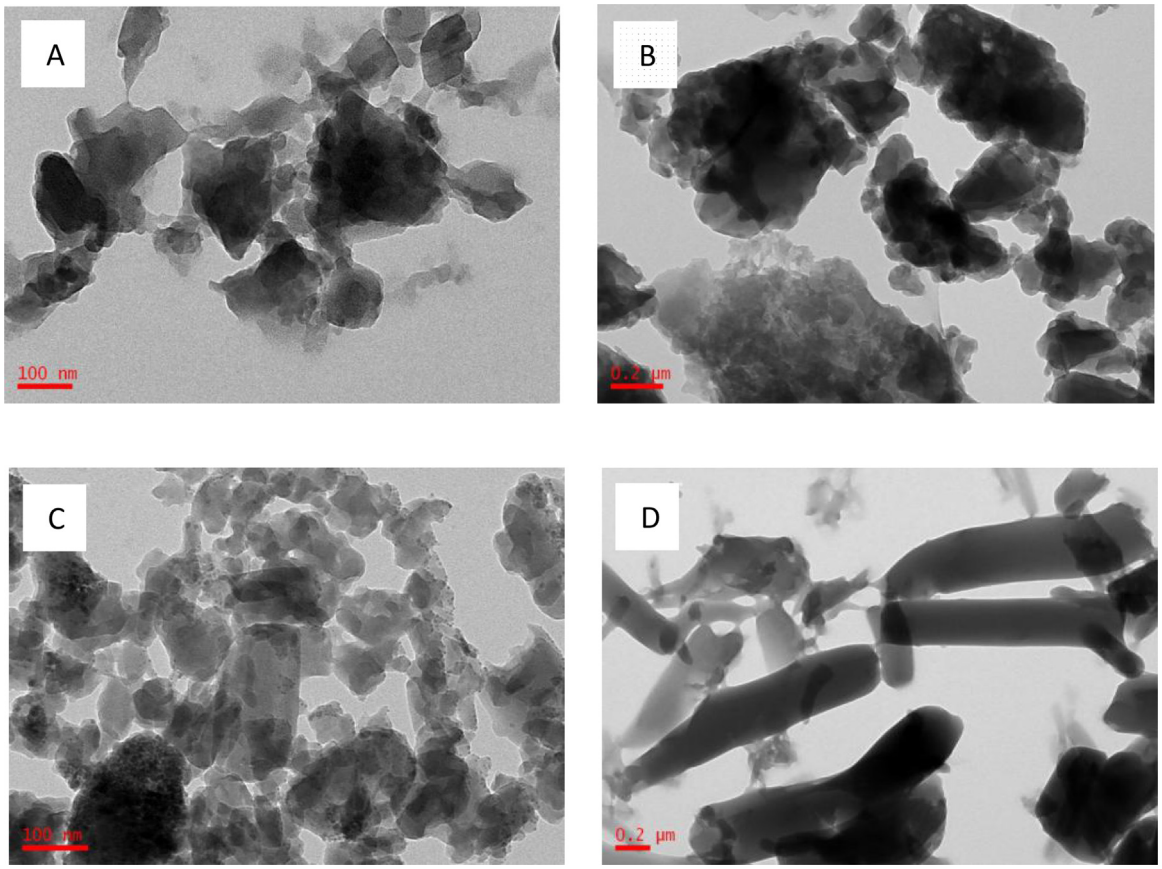

Fig. 1. TEM images of Cu-MOF samples: (A) **Cu-BTC-1**, (B) **Cu-BTC-2**, (C) **Cu(tpa)** and (D) **Cu(im)$_2$**.

while, IL generally employed as medium or catalyst [29,30], has demonstrated its potential in improving $CuCl_2$-mediated oxidation process when using 1-butyl-3-methylimidazolium chloride as the co-ligand [31]. Moreover, polyethylene-supported Fe/ionic liquid complex exhibited more excellent reactivity and recoverability than former systems [29]. Nanoscale metal-organic frameworks (NMOFs) represent a unique new family of hybrid nanomaterials [32]. Particularly, the packing of NMOFs particles can result in meso- and macropores [33], which obviously differs from the reported routes to construct mesopores using rigid slim organic linkers or large building blocks [34,35]. Furthermore, modification of the NMOF surface would significantly improve the stability and other properties of NMOFs under complex conditions [32]. Herein, we first reported the selective oxidation of anethole to anisaldehyde or 4-methoxyphenylacetone over heterogeneous Cu- and Fe-MOFs using IL as the additive. Notably, Cu-MOF catalysts are formed in the nano-submicroscale range through conventional routes, whereas Fe-MOFs are nanoscale materials obtained by a dual-ligand strategy, which could induce significant differences in MOFs morphology, structure and performance. Inspiringly, **Cu-BTC-1** and **Fe(PMA)-**based nano/submicro-sized synergistic systems were endowed with significantly enhanced activity and recyclability in the presence of amphiphilic $[C_{12}mim]Cl$ or $[C_4mim][Cys]$ derived from natural amino acid, respectively, as supported by TEM, XRD, FT-IR, DRUV-vis and UV–vis analyses.

2. Experimental

2.1. General

1-Butyl-3-methylimidazolium hydrogen sulphate ($[C_4mim][HSO_4]$), 1-butyl-3-methylimidazolium carbonate ($[C_4mim]_2CO_3$) and amino acid ionic liquids (AAILs, i.e. $[C_4mim][Cys]$, $[C_4mim][Ala]$ and $[C_4mim][Pro]$), were synthesized according to the literature [36–38]. Anethole (>99.5%, Guangxi Wanshan Spice Co., Ltd.), $[C_{12}mim]Cl$ (99%, Shanghai Cheng Jie Chemical Co., Ltd.) and other chemicals were used as purchased. FT-IR spectra of catalysts were measured using an Avatar-370 spectrometer. Thermogravimetric (TG) analysis was carried out on a Netzch Sta 449c instrument (Germany). BET surface area and other textural properties were determined by N_2 adsorption-desorption method at 77 K on a Micromeritics TriStar 3000 apparatus. Diffuse reflectance UV–vis (DRUV-vis) and UV–vis spectra were acquired with a Hitachi UV-3310 or a Shimadzu UV-2450 spectrophotometer, respectively. ^{1}H NMR spectrum was recorded using a Bruker 500 MHz NMR spectrometer. Transmission electron microscopy (TEM) image was taken on a JEM-2010 instrument (JEOL, Japan) operated at 200 kV. XRD data were collected by a Y-2000 diffractometer (Cu $K\alpha$ radiation, $\lambda = 0.154178$ nm) in the 2θ range from 2.5° to 50°. ICP-AES analysis was carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES, PS-6, Baird, USA). Fluorescence spectra were obtained using a Hitachi F-7000 fluorometer. Gas chromatography was performed on Agilent 6890 equipped with a DB-5 (30 m × 0.25 mm × 0.25 μm) column. Mass spectra were run on an America Varian Saturn 2100T GC–MS spectrometer.

2.2. Synthesis of Cu-MOFs

Cu-BTC-1, **Cu-BTC-2**, **Cu(tpa)** (**tpa**: terephthalate) and **Cu(im)$_2$** (**im**: imidazolate) were prepared by literature methods [39–42]. Details about the procedures are described in the Supporting information.