Catalysis Communications 43 (2014) 146–150

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Co(II) coordinated metal-organic framework: An efficient catalyst for heterogeneous aerobic olefins epoxidation

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ARTICLE INFO

Article history:
Received 31 July 2013
Received in revised form 13 September 2013
Accepted 17 September 2013
Available online 10 October 2013

Keywords:
MOFs
Oxygen
Epoxidation
Olefin

ABSTRACT

An 8-connected, linear trinuclear cluster-based microporous metal organic framework $(NH_4)_2[Co_3(Ina)(BDC)_3(HCOO)]$ (denoted as $Co_3InaBDC_3$, Ina = isonicotinate and BDC = 1,4-benzenedicarboxylate, CCDC is 935147) had been successfully synthesized by a facile hydrothermal synthesis method. The compound was extended through BDC linkers breadthwise and Ina linkers lengthways to the highly-connected framework. The $Co_3InaBDC_3$ was characterized through FT-IR, N_2 adsorption, XRD, TGA and SEM, and its characteristic structure was elucidated by single crystal X-ray diffraction. Using O_2 as oxidant, the $Co_3InaBDC_3$ was investigated as a good performed heterogeneous catalytic material for cyclooctene epoxidation. An extremely high turnover frequency ($1370\ h^{-1}$) for epoxycyclooctane was achieved, and $Co_3InaBDC_3$ exhibited excellent stabilities in 5 recycles without any loss of its catalytic performance.

1. Introduction

Epoxides are important intermediates in the synthesis of epoxide resins, plasticizers, cosmetics and fine chemicals [1–3]. Enormous progress had been witnessed in homogeneous and heterogeneous catalytic epoxidation processes of various olefins in the last three decades. By comparing different oxidation methods, the oxidant utilized in the transformation defines the practicality and generality of the method [4–8]. Among the various oxidants, molecular oxygen is undoubtedly the most ideal oxidant in the selective oxidation, however, there still remain great challenges in the epoxidation process involved in molecular oxygen [2,9–11]. Since the pioneering work of 'Mukaiyama' epoxidation process based on cobalt salts using molecular oxygen as the oxidant and aldehydes as co-reactant [12,13], thus Co-containing materials catalyzed epoxidation methods have been widely developed [14–16]. The heterogeneous catalyst based-Co^{II} can be easily separated, recovered, and reused from reaction mixtures, making the processes more cost effective [17–20]. Metal-organic frameworks (MOFs) are crystalline porous materials with high surface area, large pore volume, and high stability [21,22]. Among them, cobalt(II)-containing MOFs situated in a four- or five-fold coordination environment which can be employed in heterogeneous catalytic epoxidation processes are of particular interest, because of their well-maintained active sites and associated catalytic functionality [23–25]. However, only very few works have been reported involved in using cobalt(II)-containing MOFs as heterogeneous catalysts for the epoxidation of olefins.

In our previous work, we reported a onefold Co-containing zeolitic imidazolate framework material (Co-ZIF) catalyst [26], a high TOF (638.3) was achieved in the aerobic epoxidation of cyclooctene with O_2. By contrast, more regulated constructed crystalline MOF catalysts as well as their strictly regular surroundings may exhibit better performance in this abovementioned catalytic process. Herein we synthesize a Co-containing MOF catalyst with both of Co unsaturation active site and better regulated crystalline structure than Co-ZIF reported before. In the epoxidation of cyclooctene with O_2, this catalyst exhibits excellent catalytic performance in the presence of *i*-butyraldehyde with a satisfactory TOF of 1370, which is the highest value that has been reported so far in the epoxidation of cyclooctene with MOF as the catalyst (Table S1) [14,27–29].

2. Experimental

2.1. Catalyst synthesis

A mixture of 0.15 g $Co(NO_3)_2 \cdot 6H_2O$ (0.5 mmol), 0.08 g BDC (0.5 mmol), 0.06 g Ina (0.5 mmol) and DMF (10 mL) was stirred in air, then, adjusted pH to 7.8 with ammonia (25 wt.%). The resulting solution was transferred into a Teflon-lined Parr bomb, heated up to 150 °C for 65 h, cooled down to 100 °C for another 7 h programmatically. Purple hexagonal-plate crystals were obtained (62% yields based on Co). As-prepared catalyst was activated under 150 °C vacuum oven to remove

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http://dx.doi.org/10.1016/j.catcom.2013.09.014

solvents and the unstable formic acid, thus, an active Co site was exposed (Fig. S1). Elemental analysis (%): calc. for $C_{31}H_{17}Co_3NO_{19}$: C, 42.26; H, 1.93; N, 1.6; found (%): C, 42.15; H, 1.95; N, 1.58.

2.2. Catalytic reaction

In a typical experiment, 4 mg catalyst, 0.88 g (8 mmol) cyclooctene, 2.31 g (32 mmol) *i*-butyraldehyde, 0.05 g biphenyl (internal standard) and acetonitrile (16 mL) were added into the flask. The flask was fixed into a Teflon-lined stainless-steel autoclave, which was charged with O_2 to 0.2 MPa. The autoclave was put into a 35 °C water bath and reaction mixtures were stirred vigorously for 1.5 h. Liquid phase was determined by a gas chromatography (Agilent GC 7890), which was equipped with SE-30 capillary column and a FID.

3. Results and discussion

3.1. Structure of $(NH_4)_2[Co_3(Ina)(BDC)_3(HCOO)]$

In Fig. 1, X-ray diffraction analysis revealed three crystallographically-independent Co centers located in the linear trinuclear subunit. Co (2) was combined by one nitrogen atom from Ina, four bridging oxygen atoms from BDC, and one oxygen atom from formic acid stem from solvent. As TGA curve shows, Co (2) could be easily activated under 150 °C. Three adjacent Co atoms formed a linear trinuclear SBUs (secondary building units). The SBUs consisted of three Co ions, six BDC and two Ina ligands. The central Co (3) atom was linked to the other two Co (1,2) atoms by four syn–syn carboxylate bridges and two O atoms in the carboxylate group to give rise to a Co_3 cluster. The other two O atom and N atom equivalents linked Co_3 cluster into a linear chain, and these reciprocities leaded to a rigid layer. This structure stood for an unusual example of an "inorganic" metal–oxygen rigid layer, which was interconnected by dicarboxylate from BDC without the existence of any hydroxyl groups [30]. Such layers were further pillared by Ina into an 8-connected 3D metal-organic framework, with the layers stacking in a triangular prism mode. Construction of 8-connected networks was severely bounded both by the number of available coordination sites and by the sterically demanding nature of many ligands, so the 8-c nets were still rare.

The permanent porosity of $Co_3InaBDC_3$ was confirmed by N_2 adsorption at 77 K. The N_2 adsorption isotherm indicated typical type-I adsorption behavior (Fig. S2), confirming the existence of the microporous structure. The BET surface area (Langmuir surface area) and pore volume were 1048.48 m^2/g (1411.10 m^2/g) and 0.525 cm^3/g, which was more considerable than those of the ZIFs. There are three types of channels in the microporous material, 1.56 nm × 1.26 nm (a axis), 1.56 nm × 1.32 nm (b axis), 1.26 nm × 1.32 nm (c axis), respectively. The size of substrate (ca. 0.3 nm) is far smaller than the pore size. The high porosity and well-regulated network made $Co_3InaBDC_3$ a good candidate for catalysis in liquid phase reactions.

3.2. Catalytic performance

In Fig. 2, the influence of temperature, pressure, catalyst amount and time course on the epoxidation of cyclooctene was investigated respectively.

At 25 °C, the conversion of cyclooctene only reached 84% even after a long time, but the reaction was almost complete (conversion was 98%) after 90 min at 45 °C, that means to say, higher temperatures obviously enhanced the reaction rate. As was shown in the figure, 35 °C was an optimized temperature, with the highest selectivity to the epoxide of 92%. Higher temperatures than 35 °C significantly decreased the selectivity of the positive reaction.

The effects of oxygen pressure on the catalytic performances of the Co-MOF were investigated a good linear relationship between the conversion of cyclooctene and the oxygen pressure (0.1 to 0.6 MPa), and the highest selectivity to epoxycyclooctane of 92% was achieved under the optimized pressure of 0.2 MPa. A control reaction was carried out under the air, no product was detected.

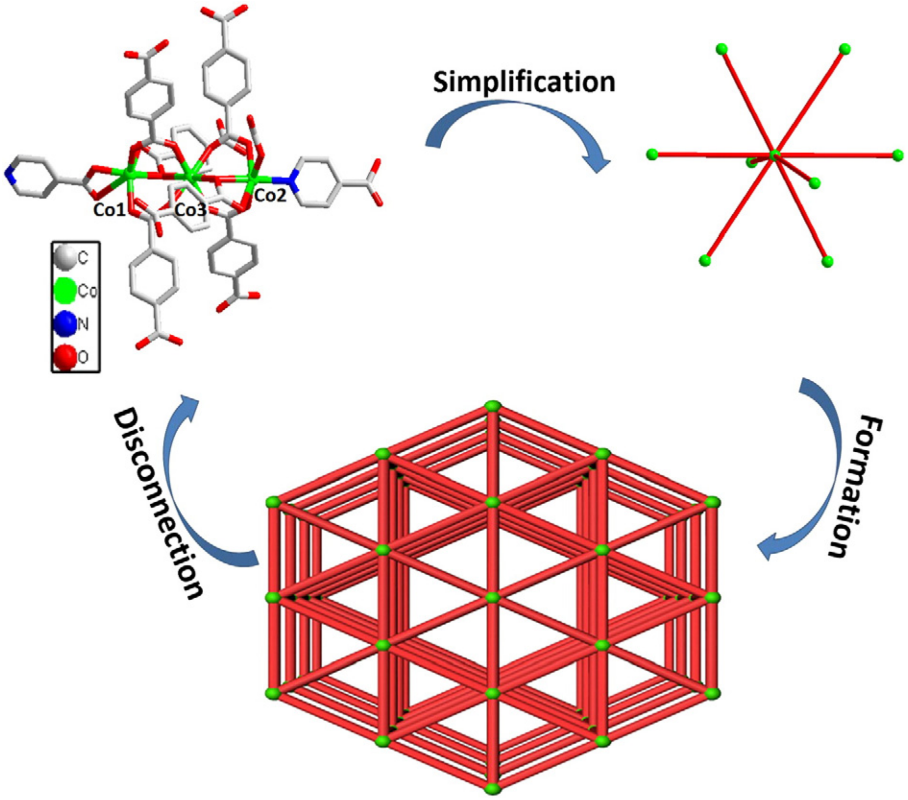

Fig. 1. Perspective views of the SBUs, simplified as an 8-connected node and the 3D topological networks in Co-MOF.