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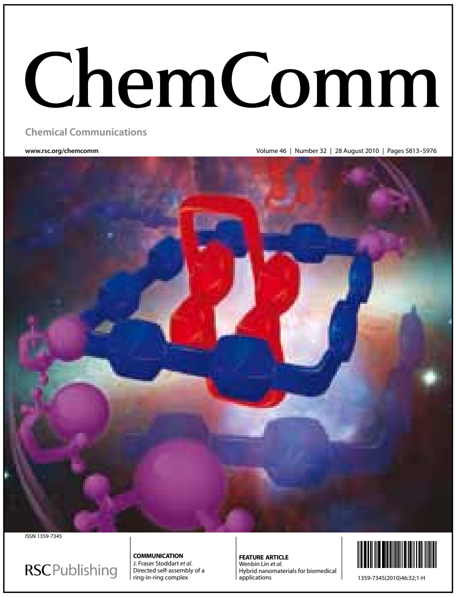

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ARTICLE TYPE

A New Layered Metal-Organic Framework as a Promising Heterogeneous Catalyst for Olefin Epoxidation Reactions

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A new layered MOF material [Co(Hoba)$_2$·2H$_2$O] (1) (H$_2$oba = 4,4'-oxybis(benzoic acid) has been synthesized and used as a highly recyclable heterogeneous catalyst for olefin epoxidation reactions. Both high conversion (96%) and high selectivity of epoxide products (96%) are achieved.

Selective oxidation of hydrocarbons to higher-value chemical feedstocks represents an important petrochemical process;[1] however, it remains a great challenge t**o** achieve high performance of these reactions. In particular, the selective oxidation of olefins into epoxides (or olefin epoxidation) has attracted tremendous attention in the scientific community because epoxides are widely used as industrially important intermediate chemicals for making valuable products such as epoxy resins, paints and surfactants. Epoxides are also versatile precursors for pharmaceutical synthesis.[2] Over the past a few decades, many homogeneous[3] and heterogeneous[4] catalysts have been developed and used to catalyze the epoxidation reactions of various olefins. Major research efforts also include the development of effective heterogeneous catalysts that can be easily recovered, reused, and separated from reaction mixtures, making the processes more cost effective. The dispersion and attachment of catalytically-active metallic nanoparticles or organometallic complexes onto polymeric or inorganic solid support materials via non-covalent or covalent interactions can generally produce effective heterogeneous catalysts for numerous reactions including olefin epoxidation.[5] This approach has also commonly been used for homogeneous epoxidation catalysts such as Co^{3+}, Fe^{3+}, Mn^{3+} and Mo^{6+} complexes. Such an immobilization process has successfully produced heterogeneous epoxidation catalysts that are as effective as their homogeneous counterparts.[5c,6] However, the syntheses of these catalysts are often costly. In addition, some of them have poor selectivity and possess randomly dispersed catalytic groups with geometries less conducive for the active sites in the solid matrix.[4,7]

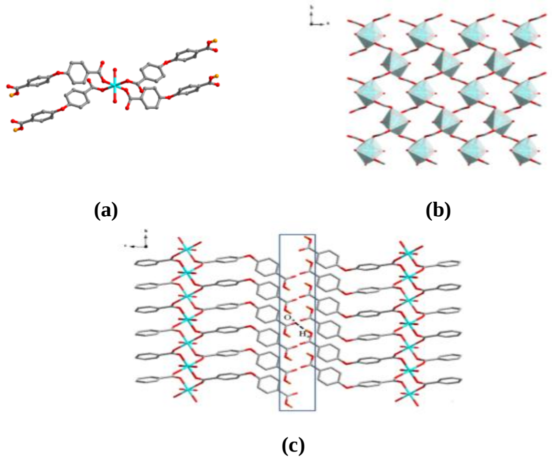
Very recently, promising heterogeneous catalytic activities of metal organic frameworks (MOFs) have been reported for a number of reactions. These reactions are catalyzed by: (1) build-in active sites (metal centers[8] or functional organic linkers[9]); and (2) grafted active sites (MOFs as solid support for grafting metal nanoparticles[10] or post-synthesis method,[11] which can generate metal binding sites). Some great advantages of MOFs as heterogeneous catalysts include interesting regioselectivity[12] or enantioselectivity,[13] which is often attributed to their large surface area, high metal content and coordination unsaturation, chirality, systematically tunable structures and composition.[13-14] These multifunctional properties make MOFs especially suitable as self-supported heterogeneous catalysts with built-in active metal centers that can readily be modified. MOFs containing unsaturated metal coordinate sites are of particular interest and have been employed in numerous catalytic reactions because of their Lewis acidity and associated catalytic functionality,[14a,14d,15] well-organized and well-maintained active sites.

To the best of our knowledge, only very few MOFs have been reported as self-supported catalysts for epoxidaion of olefins.[16] Spodine and co-workers obtained a 24% conversion of styrene and 71% selectivity to styrene oxide using a 2D MOF ([Cu(H$_2$btec)(bipy)]$_\infty$ as the catalyst.[16d] In another recent work by Koner and co-workers, 1D lanthanide MOF catalysts gave a 92% conversion of styrene with 41% yield of styrene oxide in 24 h[16e]. While these examples illustrate that MOFs are capable of catalyzing olefin epoxidation reactions, most of them are unable to simultaneously give both high conversion and high selectivity to epoxide product. We have laid our focus on the development of the Co(II) MOF catalyst not only because Co(II) cations are well known for their catalytic functions in the oxidation of olefins[7,17] because of their excellent oxygen transferring ability,[18] relatively high abundance and low cost, but also because very few Co(II) based MOF catalysts have been tested for olefin epoxidation.[19] Here, we report a new two-dimensional (2D) layered MOF structure, [Co(Hoba)$_2$(H$_2$O)$_2$](H$_2$oba = 4,4'-oxydibenzoic acid) (**1**) and its catalytic activity in olefin epoxidation reactions.

The pure-phase crystals of **1** were grown under hydrothermal conditions from a reaction between Co(NO$_3$)$_2$·6H$_2$O and H$_2$oba in 1:2 molar ratio in 10 mL distilled water and in the presence of triethylamine (TEA). The latter was used to adjust the pH to ~7.00. The reaction at 120 °C for 3 days afforded plate-like pink crystals, which were characterized by single crystal X-ray diffraction method. Compound **1** crystalizes in triclinic crystal system, space group P-1. The primary building unit (PBU) is shown in Figure 1a. All the cobalt atoms in **1** are octahedrally coordinated to four oxygen atoms from carboxylate groups in the equatorial positions and two oxygen atoms from water molecules in the axial positions. Each cobalt atom is connected to the four neighboring cobalt atoms via the bidentate carboxylate groups from oba ligands to form a 4^4 brick-like 2D layer (Figure 1b). Only one carboxylic acid of each oba ligand is deprotonated (Figure 1a). The undeprotonated carboxylic groups point outward from both sides of the Co(Hoba)$_2$ layer and form hydrogen bonds between the adjacent layers (Figure 1c).

Thermogravimetric (TG) analysis shows a weight loss of 6.0 wt% for **1** in the range of 110 °C to 160 °C upon heating. The weight loss can be assigned to the coordinated water molecules in **1** and matches very well with the theoretically calculated amount

(5.9 %) based on the crystal structure. The water-free sample **(1')** is thermally stable up to 300 °C, and starts to decompose at higher temperatures. **1'** can also be generated by heating the as-made sample **1** at 150 °C under vacuum for 2 h. The powder X-ray diffraction (PXRD) pattern of the sample taken immediately after removal of water resembles that of the as-made sample, except a shift of the major peaks to lower angles (see Supporting Information, SI, Figure S2), which indicates an expansion of the framework in the c direction. This suggests that the overall framework is very robust due to the strong hydrogen bonding between carboxylic groups from the adjacent layers (Figure 1c), while the 2D layers are fairly flexible, making them readily accessible to the substrate molecules. A color change was observed from the as-made sample (**1**, pink) to the water-free sample (**1'**, purple). The former can be readily regenerated from the latter by simply immersing the sample in water and stirring for 6 h at room temperature. Thus, the conversion between the two can be confirmed by either the change in color or by the PXRD patterns (see SI, Figure S1).

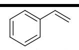
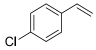
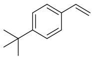
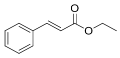
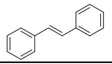

(a) (b)

(c)

Figure 1. (a) The PBU and the coordination around Co(II); (b) the 4^4 brick-like 2D layer parallel to the ab plane (the light turquoise polyhedral represent the octahedral coordination around Co(II). Benzene rings of the oba ligands are deleted for clarity; (c) the layered structure packed along the c axis and the outlined area indicates the hydrogen bonding section between the two adjacent layers. Color scheme: Co turquoise; C gray; O red; H orange; and all the hydrogen atoms are deleted for clarity except those on the undeprotonated carboxylate groups).

The catalytic activity of **1'** in the "solvent-free"[20] epoxidation reactions of styrene (Scheme S1) yielded the highest styrene conversion (96%) and selectivity (96% to epoxide) compared to reactions in various other solvents (see Table S2). This is due to the better interactions between the catalyst and substrates when the concentration of reactants is very high under such conditions. Also, **1'** gives better performance than **1** because of the presence of highly reactive open Co(II) centers (Lewis acid sites) in **1'** (see Table S1). In order to further explore the versatility of the 2D MOF as a selective epoxidation catalyst and the effect of substituents on the epoxidation reaction, different types of olefins were used as substrates under "solvent-free" conditions. The results are compiled in Table 1. When an electron-withdrawing group, chloride, was used as a substituent at the para-position on styrene (4-chlorostyrene), similar conversion as styrene, but lower selectivity to the epoxide product, was obtained. On the other hand, when an electron-donating group, tert-butyl, was used as a substituent on styrene at the para-position (4-tert-butylstyrene), the reaction produced lower % conversion than styrene, but similar selectivity (Table 1, Entries 2 and 3). When ethyl cinnamate was used as a substrate, lower conversion (69%) compared to styrene but high selectivity (ca.100%) was obtained (Table 1, Entry 4). When trans-stilbene was used as substrate, the reaction gave the same selectivity (ca.100%) as ethyl cinnamate but higher conversion (86%) (Table 1, Entry 5). The difference in the conversion between Entries 1 and 3, as well as between Entries 4 and 5, may be attributed the electronic and steric effects of the substutients at the double bond.[21]

Table 1. Epoxidation of various olefins under "solvent-free" condition by **1'**. [i]

Entry	Substrates	Conversion (%)	Selectivity (%)	
			A[j]	B[k]
1		96	96	4
2		96	65	35
3		47	94	6
4		69	ca.100	0
5		86	ca.100	0

[i] Reaction conditions: Olefins: 50 mmol; TBHP (5.5 M in decane): 100 mmol; catalyst (1'): 15 mg (0.5 mol%); Chlorobenzene (internal standard): 15 mmol; Temperature: 75 ºC; and Reaction time: 6 h. [j] a = Epoxide products. [k] b = Aldehyde products. The selectivity is only based on the two major products a and b.

Metal leaching from a solid matrix[22] is an unwanted phenomenon that is not uncommon in many heterogeneous catalytic systems. Thus, to confirm the heterogeneous behaviour of **1'**, a hot filtration experiment was conducted. As a result, a 55% conversion was obtained after 2 h of reaction and another 16% of conversion was observed after removing the catalyst and running the reaction solution for another 4h (see SI, Figure S8). The latter is most likely due to non-catalytic thermal oxidation.[14b] In order to varify this, a blank reaction was carried out without adding any catalyst. After reaction for 4h, the conversion reached 18%, which matches very well with the additional amount of conversion after removal of the catalyst (16%). Likewise, the selectivity for the epoxide product in a blank reaction is ca. 80%, similar to the values obtained after the CoMOF was removed from the reaction. To further confirm the heterogeneous nature of **1'**, the catalyst was recovered and reused four times. All repeated reactions gave identical % conversion, with only slightly lower selectivity (see Table S4). The PXRD patterns of the recovered **1'** clearly suggest that its structure is well maintained after several cycles of reactions (see Figure S6). The PXRD patterns also confirm that coordination unsaturated Co(II) metal sites remain open after the reactions (see Figure S7). The small decrease in the selectivity is likely due to the reduced crystallinity of the MOF catalysts after repeated use (see Figure S6). Inductively coupled plasma optical emission spectroscopy (ICP-OES) performed on the filtrate after the 1st and the 4th reaction cycle gave a trace amount of 0.8 and 30 ppm of Co(II), respectively. The calculated weight percent as a result of possible leaching of the catalyst is ~2 wt% (after 4 cycles) and thus, may be considered negligible.[11c,23].

Finally, the possible mechanism for the reaction was also investigated. Previous reports show that two types of mechanisms were most commonly found in metal-ion catalyzed epoxidation reactions: concerted addition of oxygen and radical epoxidation.[24] To probe if radicals were involved in our reactions, a radical scavenger, butyl hydroxy toluene (BHT), was added at the beginning of the reaction, and the reaction progress was monitored. It was observed that the reaction stopped immediately upon addition of the radical scavenger (see Figure S9), which suggests that the process indeed proceeds via radical epoxidation.[24-25] On the other hand, the same reaction in the presence of oxygen clearly indicated the formation of benzoic acid and aldehyde products as a result of oxygen involvement (see Table S6). Thus, the proposed reaction mechanism is shown in SI, Scheme S2. First, reaction between Co(II)-MOF and TBHP takes place to form a Co(III)-peroxy adduct. The Co(III)-peroxy adduct then releases a t-butoxy radical and regenerates Co(II)-MOF. This is followed by a reaction between t-butoxy radical and olefin to form a t-butoxperoxy species that will further undergo migration of oxygen to form the epoxide product and t-BuOH byproduct. Furthermore, possible involvement of oxygen or t-butoxy radicals with the t-butoxperoxy species will result in some acid and aldehyde byproducts.

In summary, we have successfully synthesized and characterized a new 2D MOF material, $Co(Hoba)_2(H_2O)_{2\infty}$ **(1)**. Removal of coordinated water molecules in **1** gives rise to **1'** which is thermally stable to 300 °C. **1'** shows excellent conversion and selectivity in epoxidation of olefins, especially under solvent-free conditions, and is highly recyclable (see SI, Table S4).

Notes and references

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[§] Electronic Supplementary Information (ESI) available: syntheses and selected crystallographic data of **1**, PXRD, TG, catalytic activity, recyclability test and mechanism study results, GC-MS spectra of products and additional figures. CCDC 777415. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x

‡These authors contributed equally to this work.

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