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Short Communication

Epoxidation of alkenes with molecular oxygen catalyzed by a manganese porphyrin-based metal–organic framework

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ABSTRACT

The flexible nature of reticular assemblies and high specific surfaces of metal–organic frameworks (MOFs) offers new opportunities for the design of heterogeneous catalysts capable of industrially relevant reactions. We demonstrate the first instance of alkene epoxidation at mild conditions using molecular oxygen by a manganese porphyrin containing MOF, MOF-525-Mn [$Zr_6O_4(OH)_4(MgC_{48}H_{24}O_8N_4Cl)_3$]. This zirconium MOF with a manganese porphyrin catalyst shows minimal deactivation over long periods and maintains its structure and high activity after multiple catalytic cycles. Kinetic studies of styrene epoxidation are in agreement with theoretical and experimental studies of homogeneous reactions with the same porphyrin unit, suggesting that the heterogeneous catalyst operates according to a similar mechanism as its homogeneous counterpart.

Here, metal–organic frameworks (MOFs) are extended crystalline structures comprising metal clusters joined by organic links [1]. Due to the tunability of the reticular framework, MOFs may be designed and synthesized for specific catalytic reactions. Heterogenous MOF catalysis [2] was demonstrated in a number of reactions including hydrogenation [3], oxidation [4], and Knoevenagel condensations [5]. Recently, MOFs with metalloporphyrin linkers have been synthesized and their catalytic applications explored [6–8]. Industrially-viable catalytic MOFs are still unknown due to framework degradation upon exposure to harsh conditions [9].

Epoxidation reactions are important to the chemical industry as oxides of small alkenes are produced in million ton quantities each year and are used as starting points for the production of common chemicals such as polyether polyol and ethylene glycol [10,11]. The catalysis of epoxidation reactions at mild conditions using molecular oxygen would be an important development. This study demonstrates the epoxidation of several alkenes with molecular oxygen by a manganese porphyrin containing MOF (Scheme 1).

Molecular oxygen, commonly used in industrial catalysis, is an ideal oxidant for epoxidations due to its low cost and environmentally friendly nature [12]. Earlier studies involving homogenous epoxidation of alkenes using manganese porphyrin show high reactivity when using molecular oxygen as the oxidant [13]. While epoxidations in MOFs using molecular oxygen have been reported [14], thus far, only low conversion rates and leeching of embedded catalysts have been shown. This article details a zirconium MOF with a manganese porphyrin active site which uses molecular oxygen for enhanced catalytic conversion rates and decreased leeching of catalytic species during epoxidation.

Heterogeneous catalysts eliminate the need for steps to separate product from catalyst. The immobilization of homogeneous catalysts has been a long-standing problem in catalysis and MOFs could be useful platforms to this end. We sought to incorporate this high catalytic activity into an extended framework by selecting the MOF-525 structure for its potentially high density of catalytically active sites and the high thermal and chemical stability of the zirconium secondary building unit [15]. While other catalytically-active porphyrin-containing MOFs have been reported [16–18], this is the first instance where a porphyrin MOF uses molecular oxygen to catalyze epoxidation of alkenes.

The synthesis and structure of the new MOF, termed MOF-525-Mn [$Zr_6O_4(OH)_4(MgC_{48}H_{24}O_8N_4Cl)_3$] [see supporting information (SI) for detailed synthetic procedure], is analogous to a previously reported MOF [19] where zirconyl chloride octahydrate (12.5 mg, 0.037 mmol) and Mn(III) meso-tetra (4-carboxyphenyl) porphine chloride (TCPP-Mn) (2.5 mg, 0.0028 mmol) were added to N,N-dimethylformamide (DMF, 10 mL) in a 20 mL scintillation vial and sonicated for 30 min. After sonication, acetic acid (2.5 mL) was added to the vial and heated

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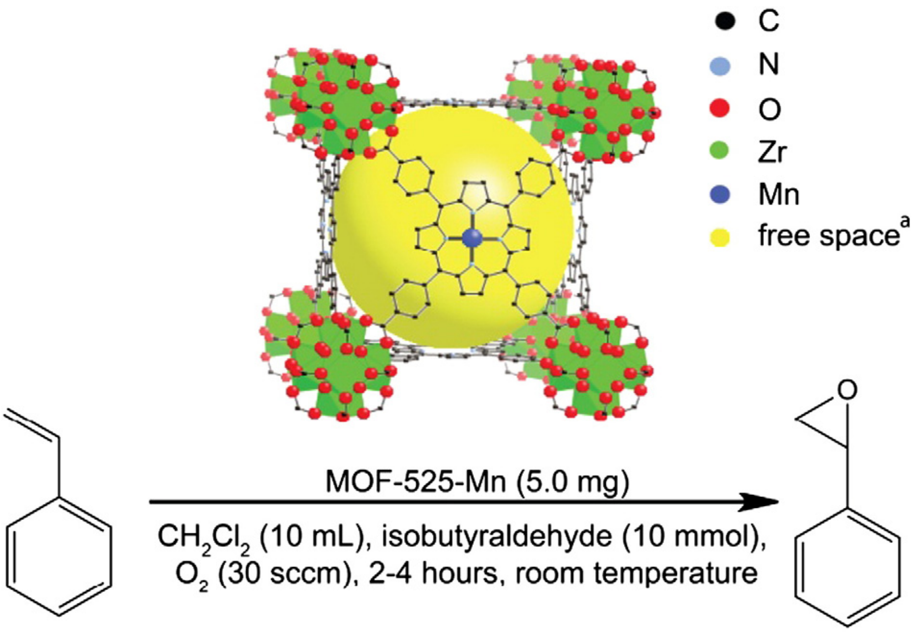


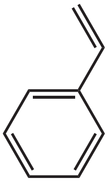
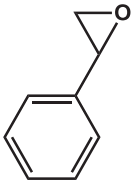
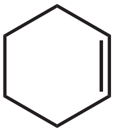
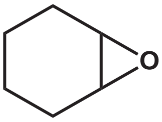
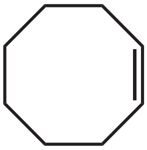
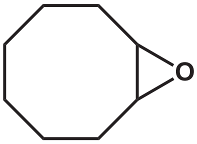
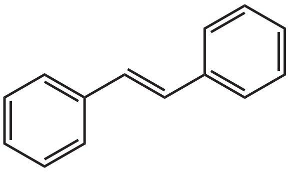
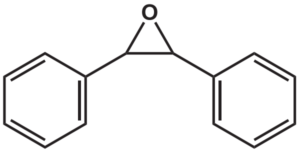
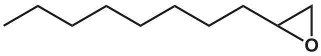
[a] Free space in the pore is illustrated by a yellow sphere that contacts the van der Waals radii of the framework atoms

Scheme 1. Epoxidation of styrene using MOF-525-Mn and molecular oxygen.

to 65 °C for 72 h to form MOF-525-Mn. The structure of MOF-525-Mn was confirmed by coincidence of the observed power X-ray diffraction (PXRD) with the simulated pattern (see SI) and has a pore size of 19 Å. Full manganese metal loading in the framework was confirmed by UV–vis spectroscopy and inductively coupled plasma atomic emission spectroscopy (ICP–AES) (see SI). N_2 adsorption isotherm measurements at 77 K revealed a Brunauer–Emmett–Teller (BET) surface area of 1850 m^2/g (see SI).

Reaction conditions were selected based on a previously published work involving homogenous manganese metalloporphyrins [20], with

Table 1
Epoxidation of alkenes catalyzed by MOF-525-Mn and free TCPP-Mn with molecular oxygen and isobutyraldehyde.

Reactant	Product	Reaction time (h)	Conversion MOF-525-Mn (%)	Yield MOF-525-Mn (%)	Yield free TCPP-Mn (%)
		2.5	99	82.8 ± 0.2	97.2 ± 0.1
		2.0	99	96.9 ± 0.1	97.1 ± 0.2
		3.0	99	96.8 ± 0.3	97.2 ± 0.1
		4.0	74	70.0 ± 0.1	84.5 ± 0.2
		4.0	75	67.9 ± 0.2	90.3 ± 0.3