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.

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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).
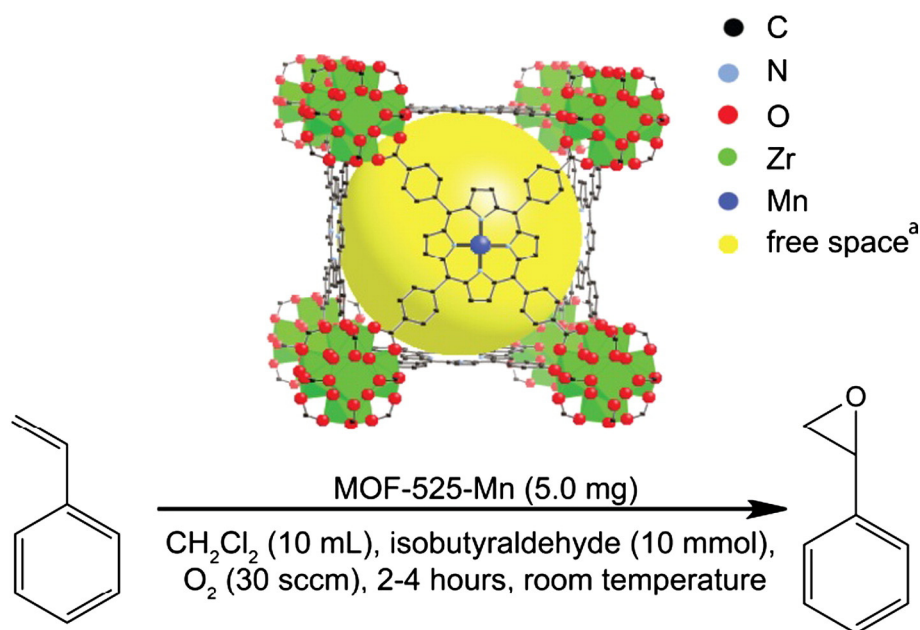
Molecular oxygen, commonly used in industrial catalysis, is an ideal oxidant for epoxidations due to its low cost and environmentally friendly nature [12]. Earlier studies involving homogenous epoxidation of alkenes using manganese porphyrin show high reactivity when using molecular oxygen as the oxidant [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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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

the exception that in our heterogeneous system the MOF catalyst could easily be separated from the reaction solution at the end of the catalytic run using a simple filtration step. The epoxidation reactions were performed by bubbling O_2 (30 sccm) through a mixture of methylene chloride (10 mL), isobutyraldehyde (0.913 mL, 10 mmol), alkene (2 mmol), MOF (5 mg) and heptane (1.0 mmol, inert internal standard) in a reaction vessel for an extended period of time. The reaction mixture was monitored using gas chromatography–mass spectrometry (GC–MS). The results for catalysis of different alkenes by both MOF-525-Mn and the free TCPP-Mn linker are summarized in Table 1, which lists the main reaction products for each alkene reactant and corresponding reaction yields and conversion rates. Note that the sizes of all alkenes and sacrificial aldehyde are small enough to fit inside the MOF pore (19 Å in diameter), allowing full access to all active sites in the framework. Some yields and conversion rates for the smaller alkenes are close to maximal for MOF-525-Mn. Ethylene and propylene were not investigated in this study due to the gas-phase nature of these reactions, requiring an entirely different reaction setup than the one used here.

In the case of styrene epoxidation, GC–MS analysis revealed a series of reaction products, with the main reaction product being styrene oxide (see SI, Fig. S6). Due to the large number of side products, we optimized the styrene reaction yield by varying reactor temperature. While this optimization technique could be applied to the other alkene reactions, we decided to focus on styrene and therefore analyzed the reaction kinetics to determine the main parameters of the epoxidation reaction pathway (Fig. 1). Industrial applications of styrene epoxidation include epoxy resins and production of chemicals such as phenethyl alcohol and styrene glycol. [21]

The reactor was modeled as a constant-volume batch reactor. Rapid stirring of the reaction mixture served to ensure homogenous mixing of all components in the reactor, and the concentration of dissolved oxygen in the reaction mixture was assumed constant due to the large and continuous flux of oxygen gas into the reaction vessel. The reaction pathway is assigned the pseudo-rate constants k_1', k_2', and k_3'. The latter are assumed to follow the Arrhenius behavior:

$$k_i'(T) = A_i(T)e^{-E_{a,i}/RT} \quad (1)$$

where $E_{a,i}$ is the activation energy for the i-th pathway, R is the ideal gas constant, T is the temperature and $A_i(T)$ is the pre-exponential prefactor. The pseudo-rate constant for styrene epoxidation, k_1', is related to the inherent rate constant, k_1, according to $k_1' = k_1[O_2]$, where $[O_2]$ is the concentration of oxygen dissolved in the solvent.

The apparent rate constants and reaction orders were computed over the temperature range 293–329 K by fitting the decline in styrene concentration over time (see SI section for details of the procedure). The pseudo-rate constants at different temperatures were used to derive the activation energy of the reaction from a fit to the Arrhenius equation. The temperature dependence of the reaction pseudo-rate constants for MOF-525-Mn was calculated from experimental data. A linearized Arrhenius plot showing the fit over the temperature range 293–329 K is found in Fig. 2. The styrene epoxidation reaction was found to be of the first order with respect to styrene, and the activation energy for the epoxidation of styrene was found to be 42.6 ± 5.7 kJ/mol. This activation energy agrees with calculated theoretical values within experimental error [22]. (We are unaware of any experimentally measured values for E_a reported in the literature at the time of writing.) The reaction order for this heterogeneous catalyst is in agreement with published results from homogeneous manganese porphyrin systems [23]. This result suggests that the manganese porphyrin heterogeneous catalyst likely operates according to a mechanism similar to its homogeneous counterpart.

The heterogeneous nature of the epoxidation reaction was confirmed by filtration. After the initial reaction of styrene, the MOF was filtered and fresh isobutyraldehyde and styrene were added to the filtrate. Using the filtrate, the reaction was run again under analogous conditions to the initial experiment and no catalytic conversion was observed. In addition, no catalytic conversion was observed if isobutyraldehyde, MOF-525-Mn, or metalated porphyrin was not present in the initial reaction mixture (see SI).

MOF-525-Mn showed minimal deactivation and maintained its structural stability and crystallinity at the end of the catalytic cycle, as evidenced by structural analysis with PXRD (Fig. 3). Leeching of manganese and porphyrin from MOF-525-Mn was investigated by performing ICP–AES and elemental analysis on the product solution after filtration. We found no evidence of leeching within experimental error of these measurement techniques (see SI). X-ray photoelectron spectroscopy (XPS) measurements indicated an oxidation state of Mn(III) within the framework and no change in oxidation state was observed after catalysis (Fig. 3). To test catalytic activity after multiple runs, several cycles of epoxidations were run back-to-back using the same MOF sample, filtering it between each run while monitoring the reaction via GC–MS.
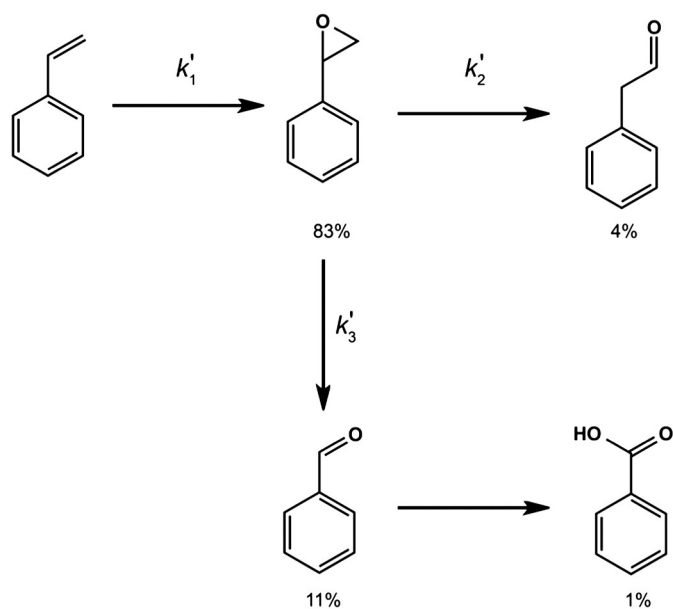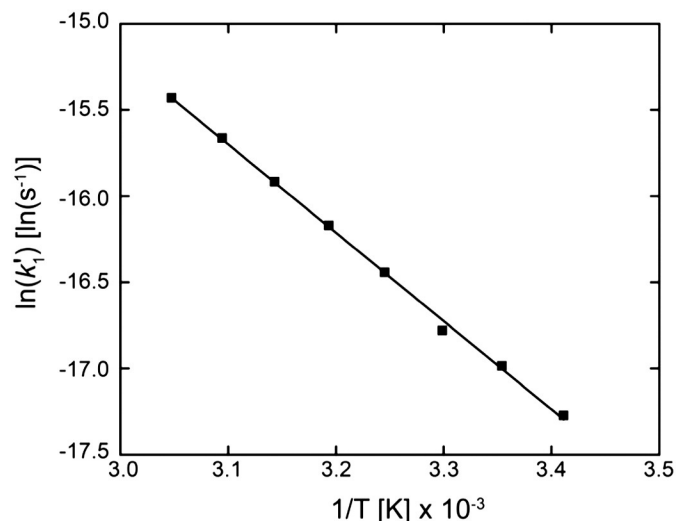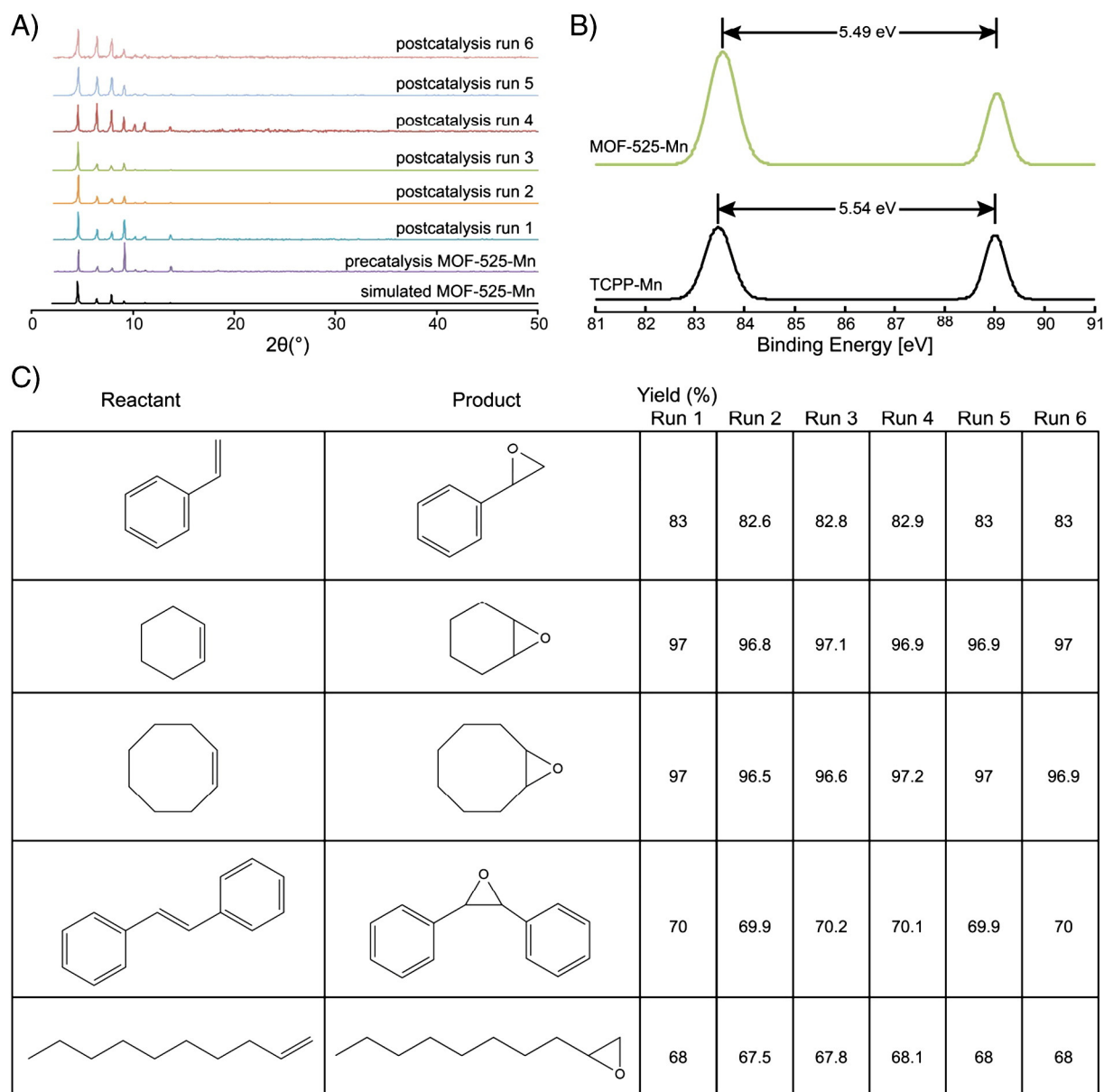

Fig. 1. Reaction pathway for the epoxidation of styrene to styrene oxide including side products. Relative yields of each species measured at equilibrium are shown as percentages.

Fig. 2. Arrhenius plot of the rate constants k_1' over the temperature range 293–329 K.

Fig. 3. Catalytic recycling of MOF-525-Mn. (A) PXRD of MOF-525-Mn after multiple catalytic runs indicates that crystallinity is maintained after 6 catalytic cycles. (B) XPS spectra for Mn 3s orbital of TCPP-Mn linker and MOF-525-Mn. The data has been fit to the sum of two Gaussian; splitting is indicative of Mn(III) and does not change after catalysis. (C) Product yield after multiple catalytic runs by MOF-525-Mn. High activity is maintained for all alkenes for 6 catalytic cycles.

High catalytic activity was maintained for all alkenes after 6 catalytic cycles (Fig. 3).

The newly developed heterogeneous catalyst, MOF-525-Mn, based on manganese porphyrin, catalyzes epoxidation reactions of alkenes using molecular oxygen. The catalyst exhibits high yields, excellent recyclability and chemical stability with respect to different alkenes tested. The ability to use molecular oxygen in heterogeneous epoxidation reactions may lead to improved strategies for industrially viable processes.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.09.040.

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