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A new heterogeneous catalyst for epoxidation of alkenes *via* one-step post-functionalization of IRMOF-3 with a manganese(II) acetylacetonate complex[†]

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A manganese(II) acetylacetonate complex has been immobilized to the metal–organic framework IRMOF-3 through a one-step post-synthetic route for the first time, providing an effective and recyclable heterogeneous catalyst for epoxidation of alkenes.

Metal-organic frameworks (MOFs), a new class of crystalline porous materials, have been generating a great deal of interest as a gas sorption medium owing to their very large surface areas and large pore volumes.1 In recent years, numerous studies have also focused on investigation of MOFs as active heterogeneous catalysts.² Previous works have revealed that chemical functionalization of MOFs by a post-modification technique plays a key role in generating catalytically active sites.³ Rowsell and Yaghi⁴ reported an amine-functionalized porous MOF, IRMOF-3, with a cubic structure having amino groups that do not take part in the formation of a 3D framework structure. Several successful attempts to chemically transform the free amine in IRMOF-3 through various postmodification techniques have been reported.^{3a,c,d,5} Rosseinsky's group, for example, described the transformation of IRMOF-3 to an imine and subsequent metallation using VO(acac)₂, with the resultant product showing low catalytic activity and stability in the epoxidation of cyclohexene.^{3a}

The transformation of alkenes to corresponding epoxides is both an important industrial technology and a useful synthetic method for a wide range of products including pharmaceuticals and agrochemicals.⁶ Manganese Schiff base complexes are known to be good homogeneous epoxidation catalysts due to their high activity and selectivity.⁷ However, problems of catalyst separation and recyclability should be addressed for these homogenous catalysts. To this end, several strategies involving immobilization of the active catalytic moiety, *viz*. to zeolites, polymer, silica, layered double hydroxide, and amine-functionalized hexagonal mesoporous silica, have been reported.⁸ In this communication, we present the first report of the binding of a manganese(π) acetylacetonate complex to IRMOF-3 through a one-step post-synthesis functionalization route. We also demonstrate that the resulting new MOF, IRMOF-3[Mn] containing Mn(acac)₂ {acac = acetylacetonate}, is a highly selective, reusable, and non-leaching catalyst for the epoxidation of several important alkenes.

The post-synthetic functionalization route for IRMOF-3[Mn] is shown in Scheme 1. IRMOF-3 was synthesized according to a procedure reported in the literature,^{4b} and kept immersed in toluene for 24 h before functionalization (see ESI†, catalyst preparation). IRMOF-3[Mn] was then prepared by dissolving Mn(acac)₂ in toluene and treating the resulting solution with IRMOF-3 crystals at 55 °C for 20 h. The material is stable in an inert atmosphere or in toluene for several months.

IRMOF-3 before and after functionalization was characterized by X-ray powder diffraction, N_2 adsorption-desorption isotherms, thermogravimetry, FTIR, X-ray photoelectron spectroscopy (XPS), inductively coupled plasma-MASS (ICP-MS), and elemental analysis. The XRD patterns of both IRMOF-3 and IRMOF-3[Mn] in Fig. 1 show well-resolved identical peaks, indicating that the original MOF framework structure was maintained with high phase purity even after the post-synthetic reaction. Furthermore, no changes in the type I N_2 adsorption-desorption isotherms (Fig. 1 inset) were found



Scheme 1 Post-functionalization route of IRMOF-3 for a Mn(II) complex.

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[†] Electronic supplementary information (ESI) available: Synthetic details, thermogravimetric analysis, FTIR (fresh and reused catalyst), ¹H NMR spectra, XPS spectra, X-ray powder diffraction (fresh and reused catalyst) and catalytic reaction procedure. See DOI: 10.1039/ c1cc00069a



Fig. 1 X-Ray powder patterns of (a) IRMOF-3 and (b) IRMOF-3[Mn] (inset shows the N_2 adsorption–desorption isotherms of (a) IRMOF-3 and (b) IRMOF-3[Mn]: \blacksquare adsorption, \Box desorption).

after post-modification of IRMOF-3, again suggesting that the structure of the parent material remained intact after functionalization. The surface area (SLangmuir) and pore volume of IRMOF-3[Mn] were 2115 m² g⁻¹ and 0.78 cm³ g⁻¹, respectively, and were reduced relative to the parent IRMOF-3 $(S_{\text{Langmuir}} = 2878 \text{ m}^2 \text{ g}^{-1} \text{ and pore volume} = 1.03 \text{ cm}^3 \text{ g}^{-1})$ as expected due to the added mass of Mn(acetylacetonate) to IRMOF-3. Similar results have been observed in other MOFs after post-modification.^{5b,9} The IRMOF-3[Mn] showed identical thermal stability to IRMOF-3 (see Fig. S1, ESI[†]). FTIR spectra of both IRMOF-3[Mn] and IRMOF-3 show intense bands in the region $1660-1550 \text{ cm}^{-1}$ (see Fig. S2, ESI⁺) due to the coexistence of carboxylato and phenyl ring vibrations.^{8c} The spectrum of the functionalized MOF exhibited a new band at 1523 cm⁻¹, which may be attributed to vibration of the acetylacetonate anion.¹⁰ The ¹H NMR spectrum of the digested IRMOF-3[Mn] (see Fig. S3, ESI[†]) shows three new peaks at 2.06, 1.94 and 1.85 ppm due to -CH₃ groups,¹¹ further confirming the presence of acac and imine-functionalized acac ligand species attached to IRMOF-3.

Further insight into the Mn(II) coordination environment of the post-modified MOF can be obtained from the XPS spectra. The XPS Mn2p region of the IRMOF-3[Mn] showed lower binding energies in comparison with the free Mn(acac)₂ complex (see Fig. S4, ESI[†]). This suggests that a different coordination environment¹² is formed upon binding of Mn to IRMOF-3, which is due to the Schiff base condensation reaction between free amine groups of IRMOF-3 and the carbonyl groups of the manganese(II) complex (Scheme 1). The comparison of the Zn/Mn ratios estimated by XPS and ICP (see Tables S1 and S2, ESI[†]) suggested that Mn complexes were preferentially bound to the NH₂ of IRMOF-3 located at the external surface due to slow diffusion of the Mn complex than its reaction rate.^{5a} ICP-MS analysis (see Table S1, ESI[†]) of IRMOF-3[Mn] revealed that the extent of binding of the manganese complex led to a final weight loading of 1.25% Mn in the MOFs, corresponding 0.23 mmol g^{-1} loading. An elemental analysis of to

IRMOF-3[Mn] was in good agreement with the formula unit $(Zn_4O)(C_8H_5NO_4)_{2.71}(MnC_{17}H_{17}NO_5)_{0.21}$.

The heterogeneous catalytic activity of IRMOF-3[Mn] was tested for the epoxidation of alkenes using molecular oxygen and aldehyde under identical conditions to those reported by Mukaiyama *et al.*¹³ The reactions are expressed in Scheme S1 (ESI[†]) and the corresponding experimental results are listed in Table 1. The products were identified by GC co-injection of commercially available standards and GC-MS.

No catalytic activity was shown by the parent IRMOF-3, and the catalytic activity of IRMOF-3[Mn] summarized in Table 1 is indicative of the presence of the active metal complex immobilized on IRMOF-3. The epoxidation of cyclohexene over IRMOF-3[Mn] using molecular oxygen (1 atm) with trimethylacetaldehyde as an oxidant precursor at 40 °C formed cyclohexene oxide with excellent selectivity (92%) and conversion (68%) (Table 1). The effect of the reaction temperature on the epoxidation of cyclohexene was investigated in a range of 25 to 55 °C (Fig. 2). The conversion gradually increased with increasing temperature while the selectivity to epoxide marginally decreased from 94 to 90%. It was also found that non-catalytic thermal epoxidation takes place in the presence of molecular oxygen and trimethylacetaldehyde, leading to 11% cyclohexene conversion at 40 °C after 6 h.

We then tested the catalytic activity of IRMOF-3[Mn] in the epoxidation of larger molecule cyclooctene using molecular oxygen and trimethylacetaldehyde. At 40 °C, cyclooctene was converted to cyclooctene oxide with lower conversion (60%) and slightly higher selectivity (96%) than cyclohexene (Table 1) under identical reaction conditions.

Styrene epoxidation was also carried out under the same reaction conditions as applied for cyclohexene in order to determine the preference for internal *versus* external double bond epoxidation. At 40 $^{\circ}$ C, styrene was converted to the corresponding epoxide with 52% conversion and 81% selectivity. The reactivity of the double bond attached to benzylic rings showed lower conversion and selectivity to

 Table 1
 Epoxidation of alkenes over IRMOF-3[Mn] using molecular oxygen^a

Cycle	Substrate	Conversion (%)	Product selectivity (%)	
			Epoxide	Others
lst	Cyclohexene ^b	67.5	92.0	8.0^e
2nd	2	67.3	91.9	
3rd		67.4	92.0	
4th		67.4	91.9	
1st	Cyclooctene ^c	60.2	95.8	4.2
2nd	•	60.3	95.7	
3rd		60.3	95.8	
1st	Styrene ^d	52.3	80.7	19.3 ^f
2nd	2	52.1	80.6	
3rd		52.2	80.7	

^{*a*} Reaction conditions: 1 mmol substrate, 2 mmol trimethylacetaldehyde, 0.015 g catalyst, 5 ml toluene, molecular oxygen (1 atm), temperature 40 °C and 6 h. ^{*b*} Without catalyst (in the presence of molecular oxygen and trimethylacetaldehyde) conversion = 10.9%. ^{*c*} Conversion = 9.3%. ^{*d*} Conversion = 9.8%. ^{*e*} 2-Cyclohexen-ol (0.9%), 2-cyclohexen-1-one (3.6%), 1,2-cyclohexenediol (3.5%). ^{*f*} Benzaldehyde (6.5%), benzyl alcohol (12.8%).



Fig. 2 Effect of temperature on the catalytic activity of IRMOF-3[Mn] using molecular oxygen (1 atm) and trimethylacetaldehyde in toluene (reaction conditions: 1 mmol cyclohexene, 2 mmol trimethylacetaldehyde, 0.015 g catalyst, 5 ml toluene, and 6 h).

epoxide than in the other two cyclic alkenes, cyclohexene and cyclooctene.

In order to asses the stability of IRMOF-3[Mn], epoxidation reaction was tested by performing repeated reaction cycles under the same reaction conditions. At the end of each reaction cycle, the catalyst was recovered by simple decantation of the solution mixture followed by washing with a solvent (5 \times 10 ml). After being immersed in the solvent for 12 h and dried at 90 °C under vacuum for 12 h, the catalyst was reused. As shown in Table 1, conversion and selectivity to epoxide were almost identical irrespective of the number of cycles performed. Further confirmation on the stability of Mn in MOF was made through a hot filtering experiment (see Fig. S6, ESI[†]). No manganese in the filtrate after the reaction was detected by ICP measurement. The X-ray powder diffraction pattern and FTIR spectra of the solid catalyst after reuse were also indistinguishable from those of the fresh catalyst (see Fig. S2 and S7, ESI[†]), suggesting that no structural deterioration or organic and metal complex decomposition occurred after catalytic reaction.

The cyclohexene epoxidation was also carried out using free $Mn(acac)_2$ (0.0002 to 0.0010 mmol) at 40 °C under identical reaction conditions. The conversion and selectivity to epoxide were much lower [42% conversion and 66% epoxide selectivity using 0.0010 mmol Mn(acac)_2] than with the IRMOF-3[Mn]. Comparison of the performances by other Mn-containing catalysts for cyclohexene epoxidation showed that the present catalyst gave much higher conversion and selectivity to epoxide than those reported for an alumina-supported Mn(acac)_2 complex.^{14a} The present catalyst also provided higher or comparable selectivity of epoxide than those previously reported for a well-known Mn(III)–salen complex immobilized to a layered double hydroxide or MCM-41.^{14b,c}

In conclusion, a new and simple approach to one-step postfunctionalization of IRMOF-3 with a manganese(II) acetylactonate complex was developed. The structure of IRMOF-3 was retained after post-functionalization. The new material, IRMOF-3[Mn], showed high activity and selectivity in the epoxidation of alkenes using molecular oxygen and aldehyde. The catalyst did not suffer from a leaching problem during catalysis and could be recycled several times without loss of activity or selectivity. In addition, the high selectivity, stability, and resistance to catalyst deactivation of IRMOF-3[Mn] demonstrated in epoxidation reactions for several important alkenes provide strong encouragement for future exploration of functionalized MOFs as useful heterogeneous catalysts.

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