

# 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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## Introduction

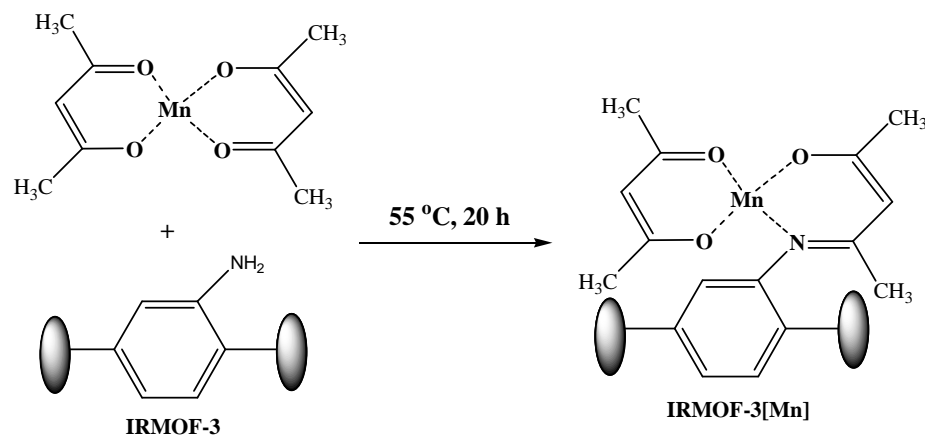
Metal-organic frameworks (MOFs), a new class of crystalline porous materials, have been generating a great deal of interest for potential application in gas storage and catalysis [1]. Previous works have revealed that chemical functionalization of MOFs by a post-modification technique plays a key role in generating catalytically active sites [2]. Yaghi et al 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 [3]. Here, we describe the binding of a manganese(II) acetylacetonate complex to IRMOF-3 through a one-step post-synthesis functionalization route and report their catalytic activity in the epoxidation of several important alkenes using dioxygen at atmospheric pressure.

## Experimental

The post-synthetic functionalization route for IRMOF-3[Mn] is shown in Scheme 1. The materials were characterized by XRD, N<sub>2</sub> adsorption-desorption isotherms, thermogravimetry, FTIR, <sup>1</sup>H NMR, XPS, ICP-MS and elemental analysis. In a typical catalytic run, 1 mmol of substrate, 2 mmol trimethylacetaldehyde, 5 mL toluene and 0.015 g of catalyst were stirred while bubbling dioxygen at atmospheric pressure and kept at the desired reaction temperature.

## Results/Discussion

The manganese(II) acetylacetonate complex was immobilized to IRMOF-3 by Schiff base condensation between the free amine groups of IRMOF-3 and the carbonyl group of the manganese(II) complex (Scheme 1). The XRD and N<sub>2</sub> adsorption-desorption isotherms indicated that the original MOF framework structure was maintained after the post-synthetic reaction.



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

The immobilized Mn-complex, IRMOF-3[Mn], was found to be effective in the epoxidation of alkenes using dioxygen (1 atm) with trimethylacetaldehyde as an oxidant precursor. The results are summarised in Table 1. The reactivity of the double bond attached to benzylic rings showed lower conversion and selectivity to epoxide than in the other two cyclic alkenes, cyclohexene and cyclooctene. The stability of the catalyst was studied by performing repeated reaction cycles under the same reaction conditions and hot filtering experiments. No leaching of the active catalyst component could be detected and the catalyst could be recycled several times without loss of performance.

Table 1. Epoxidation of alkenes over IRMOF-3[Mn] using dioxygen<sup>a</sup>

Substrate	Conversion (%)	Product selectivity (%)	
		Epoxide	Others
Cyclohexene	67.5	92.0	8.0
Cyclooctene	60.2	95.8	4.2
Styrene	52.3	80.7	19.3

<sup>a</sup> Temperature 40 °C and 6 h.

## References.

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2. Z. Wang and S.M. Cohen, *Chem. Soc. Rev.* **38**, 1315 (2009).
3. J.L.C. Rowsell and O.M. Yaghi, *J. Am. Chem. Soc.* **128**, 1304 (2006).