

Electronic supplementary information

New heterogeneous catalyst for epoxidation of alkenes via one-step post-functionalization of IRMOF-3 with manganese(II) acetylacetonate complex

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Materials

2-Aminoterephthalic acid (99%, Aldrich), zinc nitrate tetrahydrate (Merck), manganese(II) acetylacetonate dihydrate (TCI), *N,N*-dimethylformamide (99.9%, Aldrich), toluene (99.5%, Aldrich), cyclohexene (99%, Aldrich), cyclooctene (TCI), styrene (99%, Aldrich), and trimethylacetyldehyde (96%, Aldrich) were purchased and used without further purification.

Catalyst preparation

IRMOF-3 was prepared using a method previously reported in the literature.¹ The material was soaked in toluene for 24 h with the addition of fresh toluene after 6 h. The crystals were filtered off and dried at 90 °C under vacuum for 12 h. 0.05 g (0.2 mmol) of manganese(II) acetylacetonate dihydrate was dissolved in toluene (15 mL) and 0.115 g (ca. 0.4 mmol equivalent of $-NH_2$) of dry IRMOF-3 was added to the solution in a 20 mL vial. The mixture was kept in an oven at 55 °C for 20 h. The crystals were filtered off by decanting the solvent, washed with *N,N*-dimethylformamide (15 mL x 3) and toluene, and finally immersed in toluene for 24 h. The material was dried at 90 °C under vacuum for 12 h.

The synthesis reactions were also carried out by varying the temperature to 70 °C and reaction time to 48 h (both at 55 and 70 °C) to increase the Mn loading in IRMOF-3. Longer reaction time of 48 h (both at 55 and 70 °C) produced low crystalline materials with slightly increased Mn loading (1.41-1.45 wt% by ICP measurement).

Catalyst characterization

X-ray powder diffraction patterns were recorded on a Rigaku diffractometer using $\text{CuK}\alpha$ ($\lambda=1.54 \text{ \AA}$). Nitrogen adsorption/desorption isotherms were measured on a Micromeritics ASAP 2020 surface analyzer at $-196 \text{ }^\circ\text{C}$. Prior to the measurement, the sample was degassed at $120 \text{ }^\circ\text{C}$ under vacuum for 12 h. The specific surface areas of the samples were calculated both by the Langmuir and BET methods. Thermogravimetric analyses, in a range $25\text{-}700 \text{ }^\circ\text{C}$, were carried out on a TGA (Scinco S-1000) system under a N_2 flow at a heating rate of $10.0 \text{ }^\circ\text{C}/\text{min}$. The FTIR spectra were obtained on a Nicolet iS10 FT-IR spectrometer (Thermo Scientific) at ambient temperature. ^1H NMR was recorded on Varian Unity Inova FT-NMR spectrometer (400 MHz) using a solution prepared by digesting 7 mg of sample in mixture of d^6 -DMSO (500 μL) and dilute DCl (100 μL , 35% DCl). XPS measurements were carried out on a K-Alpha (Thermo Scientific). Metal contents in MOFs were evaluated using inductively coupled plasma spectrometry (ICP-OES, Optima 7300DV). Metal contents in the filtrate after catalysis reactions were determined using inductively coupled plasma-MASS spectrometry (ICP-MS, Perkin-Elmer élan 6100). C, H, and N analyses were performed using a FLASH EA 1112 elemental analyzer (Thermo Electron Corporation). The samples were dried at $90 \text{ }^\circ\text{C}$ under vacuum for 12 h prior to XPS, elemental, and metal analyses.

Catalytic reaction

The epoxidation of alkenes was carried out using molecular oxygen at atmospheric pressure in a twin-necked round flask equipped with a condenser. In a typical run, 1 mmol of substrate, 2 mmol of trimethylacetaldehyde, 5 mL of toluene, and 0.015 g of catalyst were placed in an oil bath at the desired reaction temperature while molecular oxygen was bubbled at atmospheric pressure accompanied by shaking of the mixture.

After completion of the reaction, the catalyst was filtered off and the selectivity and conversion were measured using a GC (Acme 6000, Younglin, Korea) fitted with a high performance HP-1 capillary column and a FID.

A hot filtering experiment was carried out by separating the catalyst quickly from the reaction mixture after 90 minute reaction time, and the filtrate was then maintained at $40 \text{ }^\circ\text{C}$ for an additional 270 min.

Table S1 Analytical data (wt%) for IRMOF-3 and IRMOF-3[Mn] by ICP-OES analysis^a

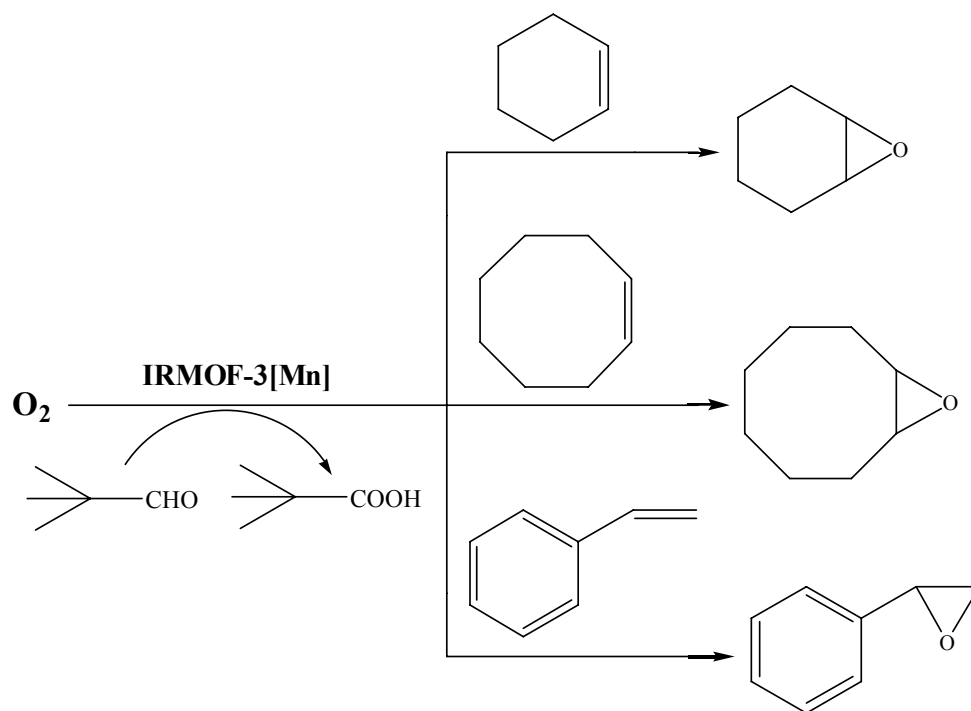
Compounds	C	H	N	Mn	Zn
IRMOF-3	35.28	1.88	5.18	-	31.91
	(35.36)	(1.84)	(5.16)	-	(32.11)
IRMOF-3[Mn]	36.48	2.11	5.01	1.25	30.22
	(36.36)	(2.07)	(4.92)	(1.33)	(30.59)

^a Calculated values are shown in parentheses. The material was dried at 90 °C under vacuum for 12 h.

Table S2 Analytical data (Atom%) for IRMOF-3[Mn] and free Mn(acac)₂ by XPS analysis^a

Compounds	C	N	O	Mn	Zn
IRMOF-3[Mn]	42.65	4.44	24.26	1.19	6.06
Mn(acac)₂	66.32	-	26.79	5.63	-

^a The material was dried at 90 °C under vacuum for 12 h.



Scheme S1 IRMOF-3[Mn] catalyzed epoxidation of cyclohexene, cyclooctene and styrene using molecular oxygen and trimethylacetaldehyde.

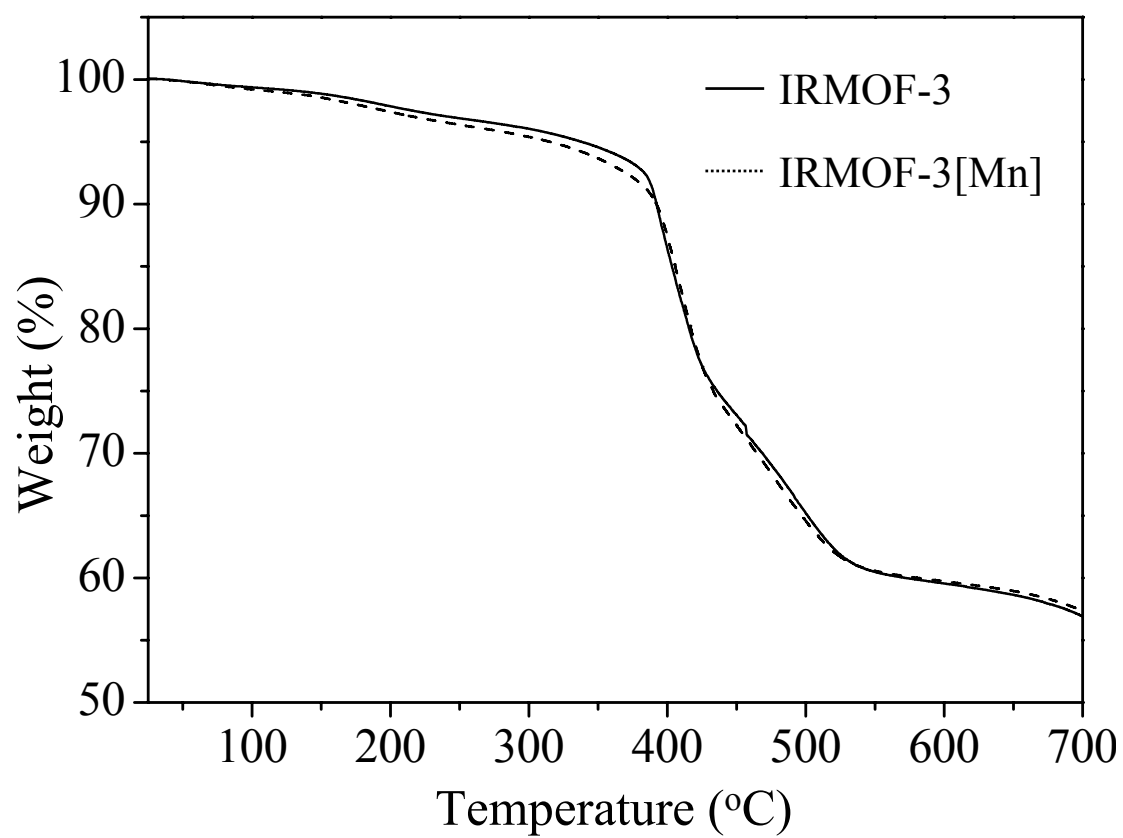


Fig. S1 TGA of IRMOF-3 and IRMOF-3[Mn].

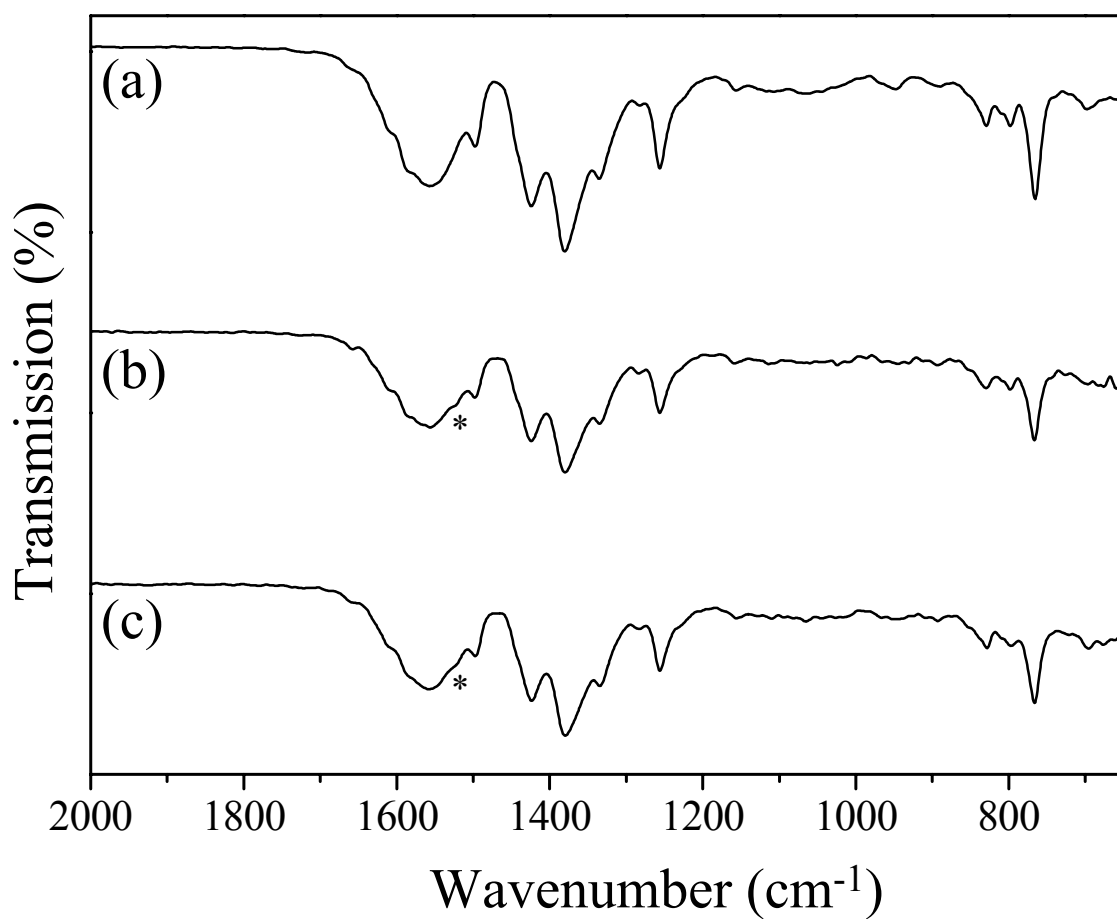


Fig. S2 FTIR spectra of (a) IRMOF-3, (b) fresh IRMOF-3[Mn] and (c) IRMOF-3[Mn] catalyst after fourth run in the epoxidation of cyclohexene.

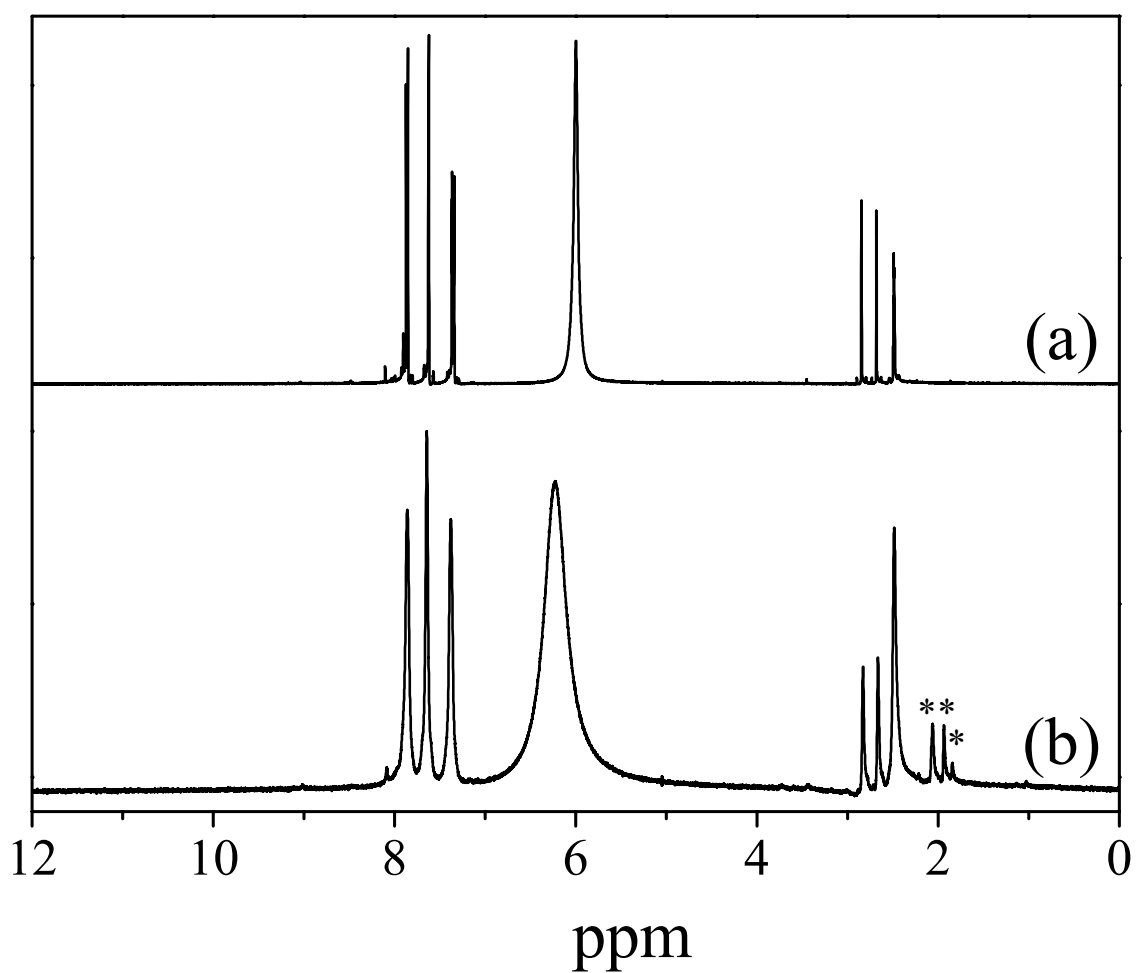


Fig. S3 ^1H NMR spectra of (a) IRMOF-3 and (b) IRMOF-3[Mn].

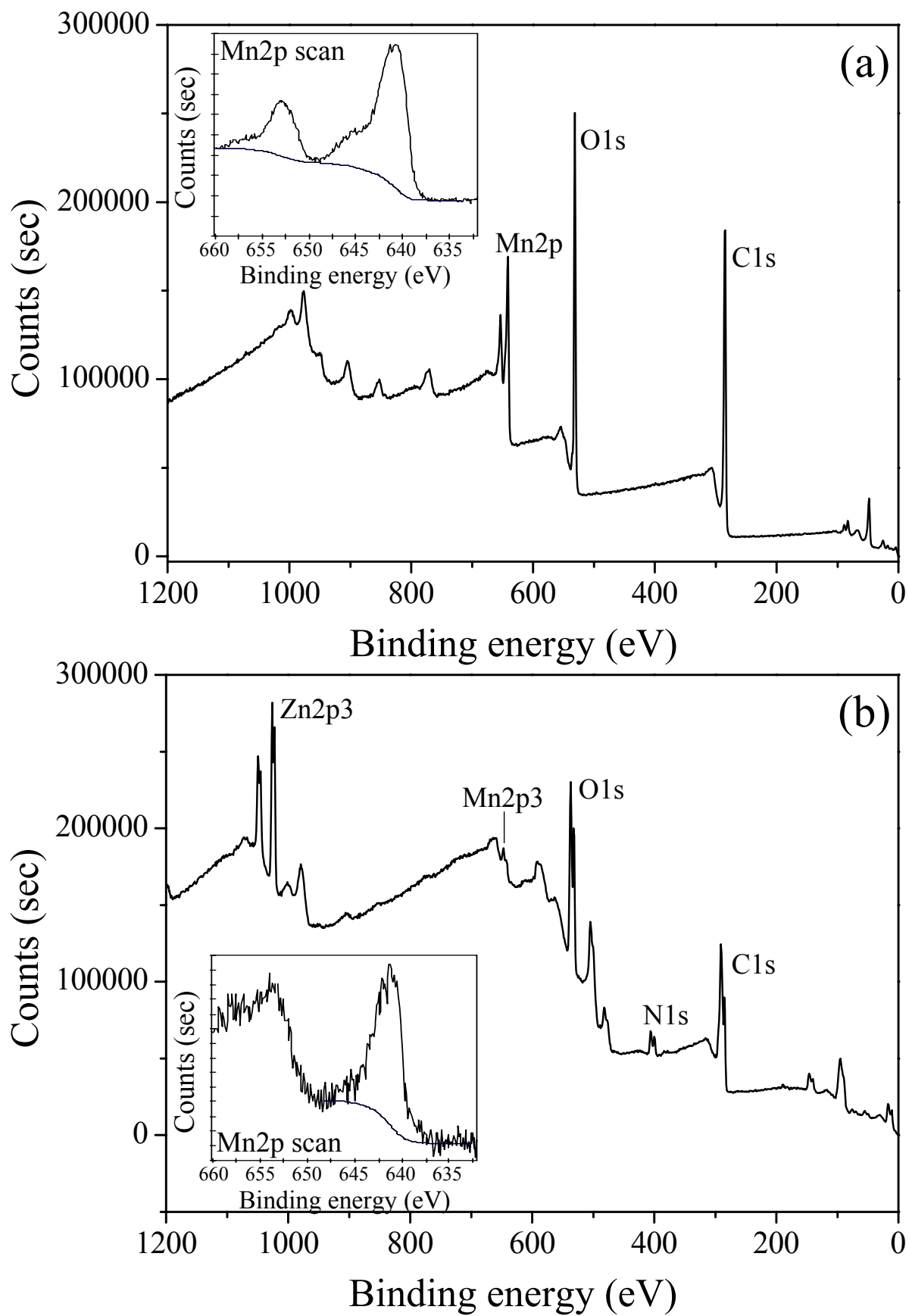


Fig. S4 XPS spectra of (a) Mn(acac)₂ and (b) IRMOF-3[Mn].

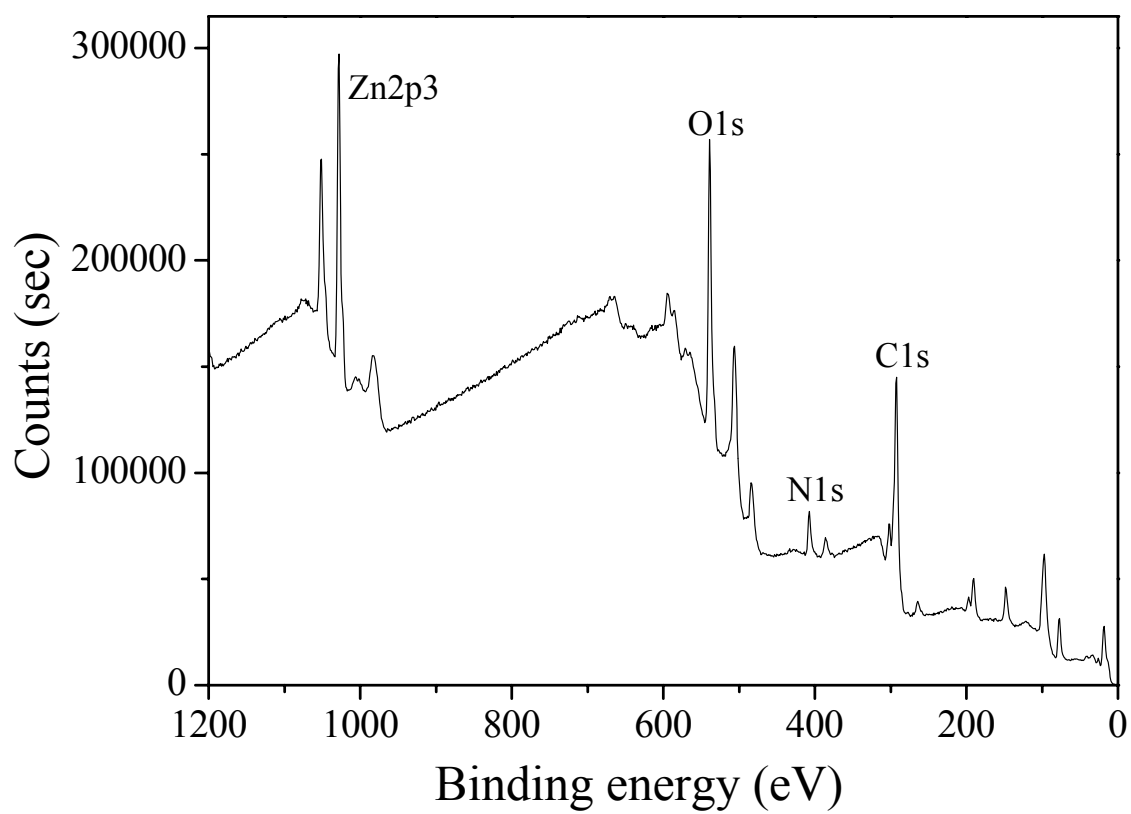


Fig. S5 XPS spectrum of IRMOF-3.

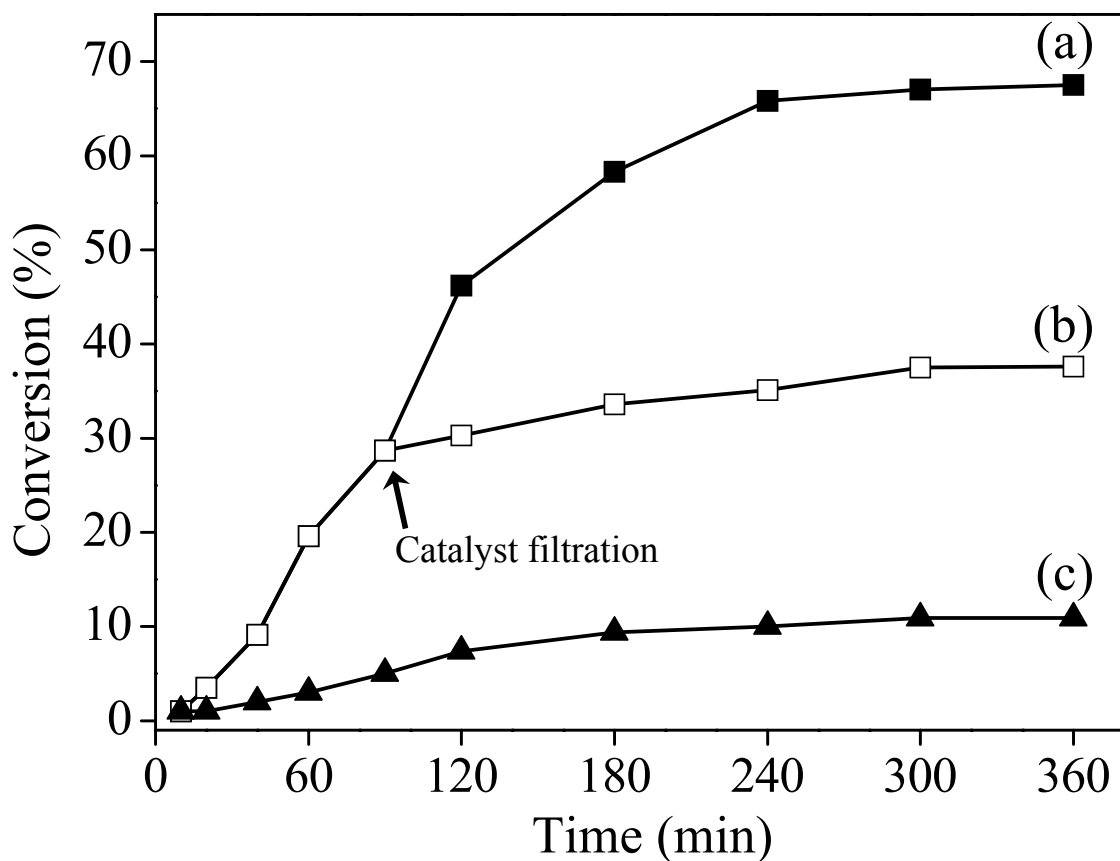


Fig. S6 Epoxidation of cyclohexene at 40 °C in toluene (a) fresh IRMOF-3[Mn] (b) filtrate (catalyst filtered off after 90 min reaction time), and (c) without IRMOF-3[Mn] (in the presence of molecular oxygen and trimethylacetaldehyde); the slightly higher conversion (3%) after hot filtration compared to the blank test after 6h of reaction appears to be attributable to the thermal reaction caused by reaction intermediates remaining in the filtrate.²

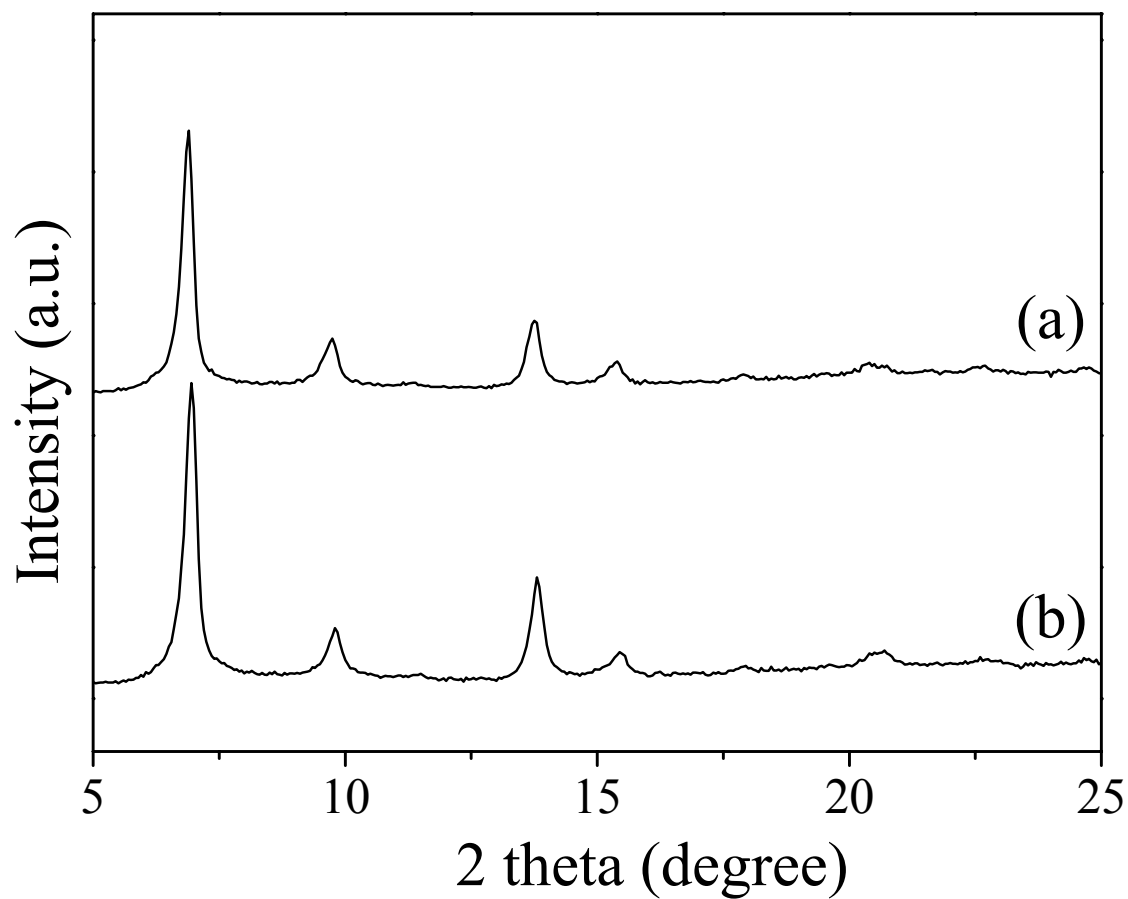


Fig. S7 XRD patterns of IRMOF-3[Mn] catalyst after (a) first run and (b) fourth run in the epoxidation of cyclohexene.

References

- [1] J.L.C. Rowsell and O.M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304.
- [2] F.X. Llabrés i xamena, O. Casanova, R. G. Tailleux, H. Garcia and A. Corma, *J. Catal.*, 2008, **255**, 220.