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ARTICLE

Post-synthesis functionalization of a zeolitic imidazolate structure ZIF-90: a study on removal of Hg(II) from water and epoxidation of alkenes

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Thiol-functionalized ZIF-90 (ZIF-90-SH) was prepared via a one-step post-synthesis route through the condensation of free aldehyde in ZIF-90 with 2-mercaptoethylamine to an imine. A subsequent reaction with manganese(II) acetate resulted in the formation of a new Mn(II)-immobilized hybrid material (ZIF-90-S[Mn]). This material was characterized by chemical analysis, X-ray diffraction, N₂ adsorption-desorption isotherms, thermogravimetric analysis and Fourier transform infrared spectroscopy, which confirmed the successful functionalization of the as-synthesized ZIF-90. ZIF-90-SH employed as an adsorbent for the removal of Hg(II) ions from an aqueous solution at room temperature exhibited an adsorption capacity of ca. 22.4 mg g⁻¹. The material showed 96-98% removal of Hg(II) ions in a low concentration range (0.1 to 10.0 mg L⁻¹). ZIF-90-S[Mn] showed good catalytic activity and selectivity in the epoxidation of several important alkenes using molecular oxygen under atmospheric pressure. Recycling and hot filtration experiments coupled with a blank test showed that epoxidation proceeded over ZIF-90-S[Mn] on the external surface of the ZIF-90 matrices, where the active Mn(II) sites were located. The catalyst could be recycled up to four times without significant loss of efficiency.

Introduction

Zeolitic imidazolate frameworks (ZIFs), a sub-family of metal-organic frameworks (MOFs), are assembled by the bonding of transition metals, such as Zn or Co, with organic imidazolate linkers in a tetrahedral arrangement. Systematic variations of the linker substituent have generated a wide range of structures with topologies identical to those found in zeolites.¹⁻⁴ More importantly, ZIFs exhibit permanent porosity, large internal surface area and uniform pore size, making them potential candidate materials for adsorption/separation²⁻⁶ and catalysis.⁷⁻¹⁰ A review dealing with the synthesis, functionalization and adsorption/catalysis application of ZIFs was recently published.¹¹ Post-synthesis modification (PSM) involves chemical modification over a pre-formed MOF host using a chemical treatment to the linkers that could not be achieved by direct MOF synthesis. The PSM of ZIFs can generate new active sites that can enhance the gas adsorption capacity or selective gas adsorption as well as active sites for heterogeneous catalysis in organic transformations.¹¹⁻¹⁹

Yaghi et al. reported an aldehyde-functionalized crystalline ZIF structure, ZIF-90, which exhibited a sodalite topology with an extended 3-D structure with pores 3.5 Å in window opening and 11.2 Å in pore size.²⁰ This material is made of uniform micropores containing -CHO groups that do not participate in the formation of a 3-D framework. The material exhibits high thermal and chemical stability. They reported the PSM of ZIF-90 through the reduction of the free -CHO groups with NaBH₄ to an alcohol and a condensation reaction with ethanalamine to an imine to form ZIF-91 and ZIF-92, respectively.²⁰

Mercury causes large scale environmental contamination, which leads to serious health problems including damage to the brain, kidneys and central nervous systems.²¹ Mercury pollution in

wastewater discharged from industries and contaminated drinking water have created great deal of concern. The maximum permissible limits of Hg(II) in wastewater and drinking water are 10 µg L⁻¹ and 2 µg L⁻¹, respectively.²² Several studies have examined the removal of Hg(II) ions from water by ionic exchange,²³ solvent extraction,²⁴ membrane separation²⁵ and adsorption.²⁶ One of the most interesting properties of mercury(II) ions is its ability to strongly interact with ligands having sulfur or nitrogen donor atoms. The selective removal of Hg(II) ions from water has been studied using a variety of functional materials over the recent years, such as porous cellulose carrier modified with polyethyleneimine,²⁷ dithiocarbamate-incorporated mono polystyrene microsphere,²⁸ hexagonal mesoporous silica with 2-mercaptothiazoline,²⁹ magnetic iron oxide nanoparticles with 2-mercaptothiazole,³⁰ thiolated cross-linked polyethyleneimine,³¹ and magnetic dithio-functionalized MCM-41 nanoparticles.³² On the other hand, there are few reports on the removal of heavy metal ions from contaminated water using MOFs. Ke et al. reported that a thiol-functionalized MOF, dithioglycol-grafted CuBTC (BTC=benzene-1,3,5-tricarboxylate), which was prepared by the coordination of dithioglycol to the unsaturated metal centers, exhibited high adsorption capacity for Hg(II) ions from water.³³

Epoxides are important intermediates for the preparation of a wide range of products including pharmaceuticals and agrochemicals.^{34,35} Manganese Schiff base complexes are attractive potential homogeneous catalysts for the epoxidation of alkenes to epoxides.³⁶ On the other hand, the difficulty in catalyst separation and recyclability should be addressed for such homogeneous systems. To overcome these problem, several strategies for attaching the active manganese complexes to zeolites,³⁷ silica through chloropropyl spacers metalated with manganese,³⁸ dicationic Mn(III) complex immobilized into montmorillonite clays,³⁹ salen-Mn(III) complex

axially immobilized into MCM-41,⁴⁰ and sulfonato-salen-Mn(III) complex into layered double hydroxide have been attempted.⁴¹⁻⁴⁴ A recent study also reported an efficient heterogeneous catalyst for the epoxidation of several alkenes over functionalized IRMOF-3, which was produced through a one-step PSM of IRMOF-3 with a Mn(II) acetylacetonate complex.⁴⁵ ZIF-90 molecular sieve membranes were successfully prepared through a post-synthesis functionalization route, which exhibited excellent H₂ separation from other gases.^{46,47} ZIF-90 was also immobilized on amino-functionalized silica fibers through PSM and applied for solid-phase microextraction of phenolic endocrine disruptors in environmental samples.⁴⁸ In addition, ZIFs were effective as a support for encapsulation of noble metals or non-noble metal nanoparticles due to its high thermal and chemical stability.¹¹ Au nanoparticles supported on ZIF-8 and ZIF-90 showed an efficient catalytic activity for the liquid-phase aerobic oxidation of benzyl alcohol and reduction of nitrophenol to respective products in good yield.⁴⁹

In this study, a thiol-functionalized ZIF-90 was prepared and evaluated for the removal of Hg(II) ions in water. This paper also describes the synthesis of a new catalytic material, in which manganese(II) acetate is bound to the thiol-functionalized MOF through a one-step PSM, as well as its catalytic activity in the epoxidation of several important alkenes by molecular oxygen at atmospheric pressure. To the best of the authors' knowledge, the application of thiol-functionalized ZIF-90 for the removal of mercury in an aqueous solution and subsequent transition metal complex formation using Mn(ac)₂ for the oxidation of alkenes has not been reported.

Synthesis

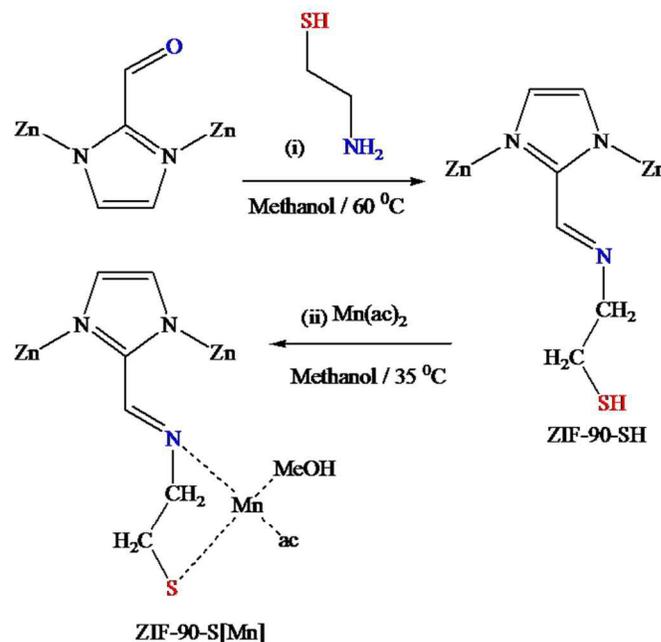
Materials

Imidazolate-2-carboxyaldehyde (99%, Aldrich), zinc nitrate tetrahydrate (Merck), manganese(II) acetate dihydrate (97%, Aldrich), 2-mercaptoethylamine hydrochloride (98%, Lancaster), *N,N*-dimethylformamide (99.9%, Aldrich), toluene (99.5%, Aldrich), cyclohexene (99%, Aldrich), cyclooctene (TCI), styrene (99%, Aldrich), and trimethylacetaldehyde (96%, Aldrich) were purchased and used as received.

Catalyst preparation

ZIF-90 (**1**) was prepared using the method reported elsewhere.²⁰ 2-mercaptoethylamine hydrochloride (0.133 g) and sodium hydroxide (0.048 g) were dissolved in 10 cm³ of methanol and the resulting solution was stirred for 15 min at room temperature. 0.10 g (ca. 0.393 mmol equivalent of -CHO) of dried ZIF-90 was added to the above solution, and the resulting mixture was heated under reflux for 24 h. The solid was filtered off and washed several times with methanol. The solid was then exchanged with fresh methanol (15 cm³ × 3) for 24 h and dried under vacuum for 24 h at 50 °C. The sample is denoted as ZIF-90-SH (**2**).

0.034 g of manganese(II) acetate dihydrate was dissolved in methanol (5 cm³). Subsequently, 0.10 g of dry ZIF-90-SH (**2**) was added to the solution in a 15 cm³ vial. The mixture was kept in an oven at 35 °C for 24 h. The crystals were filtered off by decanting the solvent, washed with methanol (15 cm³ × 3) and finally immersed in fresh methanol for 24 h. The material was dried at 50 °C under vacuum for 24 h. The sample is denoted as ZIF-90-S[Mn] (**3**).



Scheme 1 Post-synthesis functionalization route of ZIF-90 with (i) 2-mercaptoethylamine and (ii) manganese(II) acetate.

Table 1 Chemical analysis (wt%) of **1**, **2** and **3**^a

Compounds	C	H	N	S	Mn	Zn
ZIF-90 (1)	37.56 (37.60)	2.67 (2.37)	21.32 (21.92)	-	-	25.43 (25.59)
ZIF-90-SH (2)	38.51 (38.56)	4.28 (4.40)	22.49 (22.63)	17.14 (16.92)	-	17.45 (17.50)
ZIF-90-S[Mn] (3)	38.73 (38.61)	3.76 (3.78)	22.04 (22.35)	17.18 (17.05)	0.43 (0.44)	17.31 (17.35)

^aCalculated values are shown in parentheses.

Catalyst characterization

Powder X-ray diffraction (XRD, Rigaku Miniflex) was performed using CuK α ($\lambda=1.54\text{\AA}$) at $0.5^\circ \text{ min}^{-1}$. The N₂ adsorption-desorption isotherms were measured in a BELsorp-Max (BEL, JAPAN) at -196 °C. The specific surface areas of the samples were calculated by the Brunauer-Emmett-Teller (BET) method. Prior to the measurement, the sample was degassed at 50 °C under vacuum for 12 h. Thermogravimetric analysis (TGA, Scinco S-1000), in the range, 25-800 °C, was carried out under a N₂ flow at a heating rate of 10.0 °C/min. The Fourier transform infrared (FTIR, Nicolet iS10 FT-IR spectrometer, Thermo Scientific) spectra were obtained at ambient temperature. The Mn contents in the filtrate after the catalytic reactions were determined by inductively coupled plasma-MASS spectrometry (ICP-MS, Perkin-Elmer élan 6100). Chemical analyses were performed using a FLASH EA 1112 elemental analyzer (Thermo Electron Corporation). Metal contents in MOFs were measured using inductively coupled plasma spectroscopy (ICP-OES: Optima 7300DV). Prior to elemental and metal analyses, the samples were dried at 50 °C under vacuum for 24 h.

Mercury removal from water

A high concentration (1000 mgL⁻¹) HgCl₂ solution used for adsorption experiments was purchased from Aldrich. The lower

concentrations of the Hg(II) solution ($50\text{--}0.1\text{ mgL}^{-1}$) were prepared by a dilution of the measured volumes of stock solution with deionized water. The mercury adsorption capacity of the thiol-functionalized ZIF-90 was measured by introducing sample 2 to an aqueous HgCl_2 solution with constant shaking. In a typical procedure, 10 mg of **2** was introduced to a 50 mgL^{-1} HgCl_2 aqueous solution (10 cm^3) with shaking at room temperature for 24 h. After equilibrium, the material was filtered through a $0.45\text{ }\mu\text{m}$ filter membrane. The Hg contents were determined by atomic absorption spectroscopy (AA FIMS-MHS).

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 the substrate, 2 mmol of trimethylacetaldehyde, 5 cm^3 of toluene, and 0.020 g of catalyst were introduced and the reactor was placed in an oil bath at the desired reaction temperature whereas molecular oxygen was bubbled through the reaction mixture. After the reaction was complete, the catalyst was filtered off and the conversion and selectivity were measured by gas chromatography (GC, Acme 6000, Younglin, Korea) using a high performance HP-1 capillary column and a flame ionization detector (FID).

A hot filtration experiment was carried out by separating the catalyst quickly from the reaction mixture after a 90 min reaction, and the filtrate was then maintained at $40\text{ }^\circ\text{C}$ for an additional 210 min.

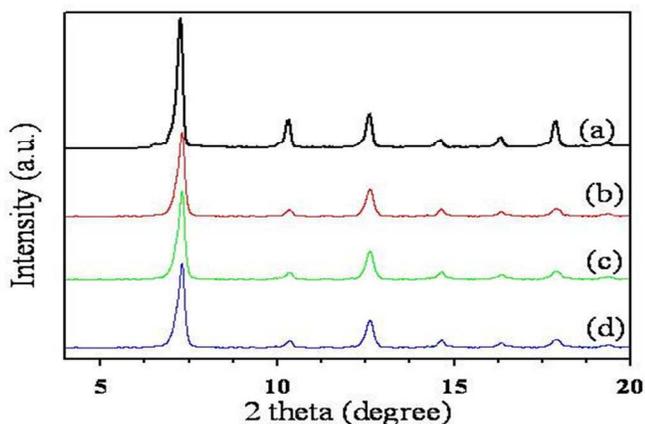


Fig. 1 Powder X-ray diffraction patterns of (a) **1**, (b) **2**, (c) fresh **3** and (d) the reused catalyst **3** after the fourth run.

Results and discussion

Synthesis

Scheme 1 presents the post-synthetic functionalization steps of ZIF-90. ZIF-90 was prepared solvothermally²⁰ and activated with methanol for three-days at room temperature prior to functionalization (see catalyst preparation). The thiol-functionalized ZIF-90, **2**, was prepared by refluxing an excess of 2-mercaptoethylamine hydrochloride in methanol in the presence of sodium hydroxide. In methanol, manganese(II) acetate dihydrate was reacted with **2** to produce **3**. The materials were stable in air and organic solvents, e.g., methanol and toluene, at elevated temperatures.

Characterization

ZIF-90 before and after functionalization was characterized by XRD, N_2 adsorption-desorption isotherms, TGA, FTIR

spectroscopy, and chemical analysis. Fig. 1 presents the XRD patterns of ZIF-90 (**1**), ZIF-90-SH (**2**) and ZIF-90-S[Mn] (**3**). The XRD patterns of all the samples were in good agreement with the data published by Yaghi et al.,²⁰ indicating that the original ZIF-90 framework structure had been maintained with high phase purity, even after modification with 2-mercaptoethylamine and the subsequent immobilization of manganese(II)acetate.

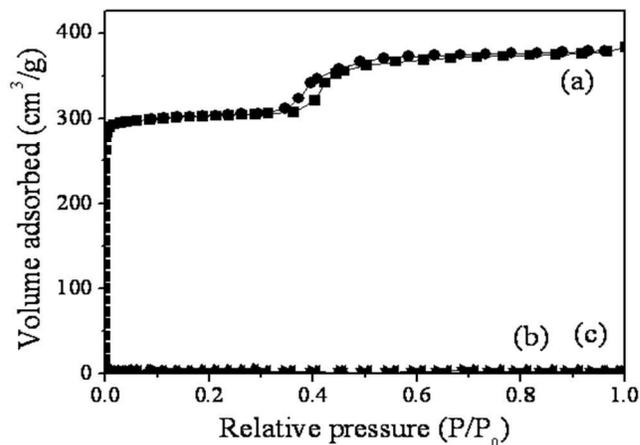


Fig. 2 N_2 adsorption-desorption isotherms of (a) **1**, (b) **2** and (c) **3**.

Fig. 2 shows the N_2 adsorption-desorption isotherms of ZIF-90 and functionalized samples. The isotherms of **1** (Fig. 2a) was identical to the data reported by Yaghi et al.²⁰ and the specific BET surface area of the obtained ZIF-90 was ca. $1250\text{ m}^2\text{g}^{-1}$. The isotherms of materials **2** and **3** (Fig. 2b and c) indicates severely blocked pore apertures due to the presence of the larger imine group formed. Similar observations have been reported in the post-synthesis functionalization of ZIF-90 with ethanolamine.²⁰

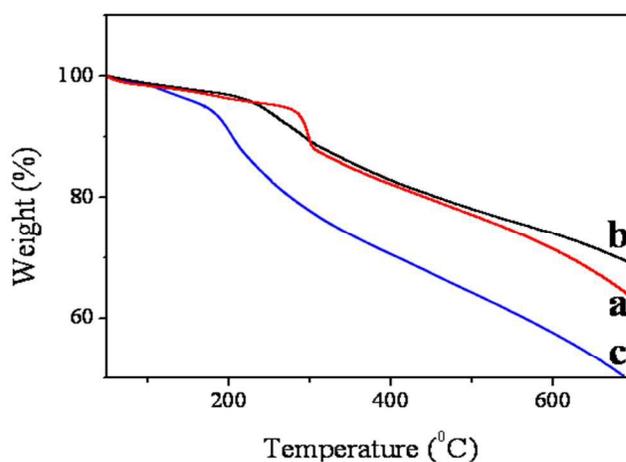


Fig. 3 TGA curves of (a) **1**, (b) **2** and (c) **3**.

Fig. 3 presents the TGA curves of **1**, **2** and **3**. The TGA diagram of the pure ZIF-90 showed a single-step weight loss; a sharp weight loss at $275\text{ }^\circ\text{C}$ due to decomposition of the network (Fig. 3a). The weight loss behaviour of the thiol-functionalized sample, **2** also showed a one-step weight loss. Collapse of the MOF framework of **2** occurred at $215\text{ }^\circ\text{C}$ (Fig. 3b). For the weight loss behaviour of **3** (Fig. 3c), the weight loss observed

up to 190 °C was attributed to the loss of coordinated methanol and acetate molecules, followed by the sharp weight loss at approximately 190 °C due to decomposition of the network. Fig. 3 shows that sample **2** was thermally less stable than the parent ZIF-90 and that **2** was in turn slightly more thermal stable than the Mn(II)-containing hybrid material **3**.

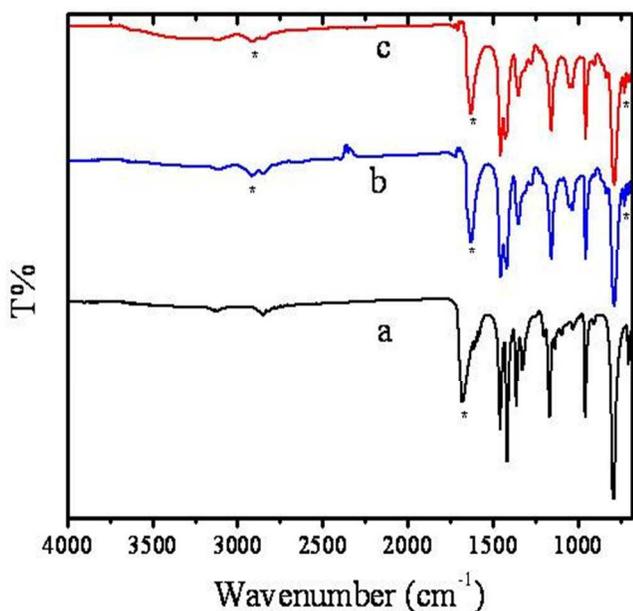


Fig. 4 FTIR spectra of (a) **1**, (b) **2** and (c) **3**.

Fig. 4 shows the FTIR spectra of **1**, **2** and **3**. ZIF-90 (**1**) exhibits a strong band at 1675 cm⁻¹ in the spectrum due to the stretching mode of the -CHO moiety (Fig. 4a).^{20,50} The -CHO vibration was absent in the spectrum of **2** and a new band appeared at ~1627 cm⁻¹ (Fig. 4b), which is due to the Schiff base condensation reaction between the free aldehyde groups of ZIF-90 and the amine groups of 2-mercaptoethylamine to form an imine.^{20,50} Further support of this condensation reaction is provided by the bands at 2917 and 720 cm⁻¹ due to the ν(C-H) and ν(C-S) vibrations, respectively.^{33,50} The FTIR spectrum of **3** shows bands at 1625, 2910 and 722 due to the presence of ν(C=N), ν(C-H) and ν(C-S) (Fig. 4c). The bands in the 1500-1350 cm⁻¹ region, which serve as a fingerprint of the acetate group,^{51,52} were not readily assignable due to the presence of ZIF-90 ring vibrations in **3**.

The amount of bound manganese in **3** was 0.08 mmol g⁻¹ according to inductively coupled plasma-mass spectrometry (ICP-MS), which is ca. 1/3 of that previously reported for a manganese(II) acetylacetonate complex bound to IRMOF-3 through the PSM developed in a previous study.⁴⁵ The lower weight loading of the Mn complexes in **3** can be explained by the differences in pore size; Mn complexes can be formed both on the external and internal surface due to the larger pore size of IRMOF-3 (~8 Å pore windows), whereas the pore aperture of ZIF-90 was 3.5 Å, which is significantly smaller than the reactant molecules, and the Mn complexes were formed on the external surface of ZIF-90 only with the inner core of MOF essentially remaining unchanged. The Zn content in **3** (Table 1) was in good agreement with the structural formula, indicating that no leaching of Zn from the MOF structure or exchange of Zn by Mn took place during the synthesis. The chemical analysis of **1**, **2** and **3** were consistent with the formula units of

Zn(C₄H₃N₂O)₂, Zn(C₆H₈N₃S)₂ and Zn(C₆H₈N₃S)_{1.97}(MnC₉H₁₄N₃SO₃)_{0.03}, respectively (Table 1).

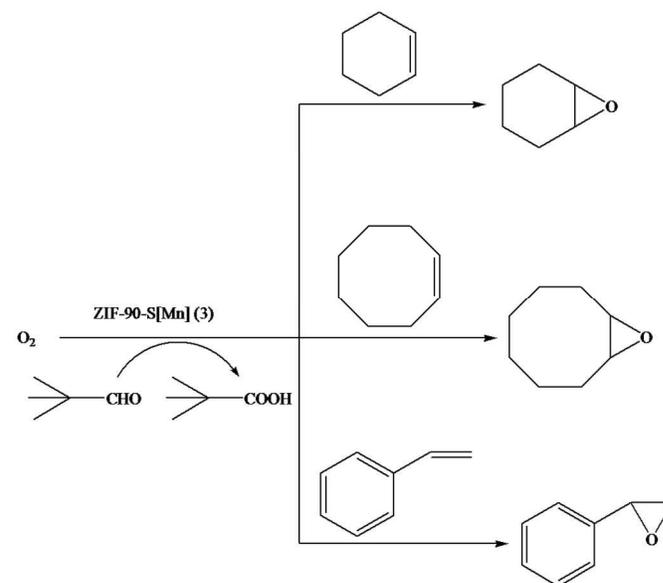
Hg(II) removal from water

The mercury adsorption capacities of the thiol-functionalized ZIF-90 were measured by mixing a weighted amount of **2** (10 mg) with 10 cm³ of an aqueous Hg(II) solution with concentrations ranging from 50 to 0.1 mgL⁻¹. Adsorption was carried out with constant shaking at room temperature for 24 h. Table 2 lists the Hg uptake of **2**. Water containing a high concentration of Hg(II) (50-25 mgL⁻¹) treated with **2** resulted in 44.9-89.7% removal of Hg(II) ions, indicating an adsorption capacity of approximately 22.4 mgg⁻¹. Table 2, shows that more than ca. 95 % Hg removal efficiency was achieved when the mercury concentration was low (0.1 to 10.0 mgL⁻¹). The XRD pattern of **2** after Hg adsorption was indistinguishable from that of the fresh material, indicating no structural deterioration or organic decomposition took place during the Hg adsorption in water solution at room temperature after 24 h. However, the possibility of slight decomposition of organic parts in the framework during Hg adsorption cannot be ruled out completely.

Table 2 Hg(II) concentration in aqueous solution before and after treating with **2**^a

Hg(II) (mgL ⁻¹)		Adsorption capacity (mgg ⁻¹)	Removal efficiency (%)
Initial	After adsorption		
50.00	27.55	22.45	44.90
30.00	7.59	22.41	74.70
25.00	2.57	22.43	89.72
10.00	0.247	9.753	97.53
1.00	0.0365	0.9635	96.35
0.10	0.0042	0.0958	95.80

^a Adsorption condition: 0.01 g **2**, 10 cm³ Hg(II) solution, 25 °C and 24 h.

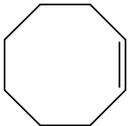
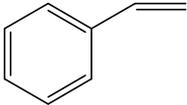


Scheme 2 ZIF-90-S[Mn] (**3**) catalyzed epoxidation of cyclohexene, cyclooctene and styrene using molecular oxygen and trimethylacetaldehyde.

Catalytic activity of the epoxidation of alkenes

The ZIF-90-S[Mn] was tested as a catalyst for the epoxidation of alkenes using molecular oxygen under atmospheric pressure. Scheme 2 and Table 3 present the reaction step and experimental results, respectively. No catalytic activity was found by ZIF-90 or ZIF-90-SH under the same reaction conditions.

Table 3 Epoxidation of alkenes over ZIF-90-S[Mn] using molecular oxygen^a

Cycle	Substrate	Conversion (%)	Product selectivity (%)	
			Epoxide	Others
1 st		65.0 ^{b,g}	77.4	22.6 ^c
2 nd		64.8	77.2	22.8
3 rd		64.8	76.8	23.2
4 th		64.8	77.0	23.0
1 st		61.7 ^c	80.2	19.8
4 th		61.5	80.0	20.0
1 st		53.8 ^d	81.2	18.8 ^f
4 th		53.5	81.0	19.0

^a Reaction conditions: 1 mmol substrate, 2 mmol trimethylacetaldehyde, 0.020 g catalyst, 5 cm³ toluene, molecular oxygen (1 atm), temperature 40 °C and 5 h. Without catalyst (in the presence of molecular oxygen and trimethylacetaldehyde): ^bconversion = 10.4%; ^cconversion = 9.3%; ^dconversion = 9.8%. ^e2-Cyclohexen-ol (1.4%), 2-cyclohexen-1-one (1.7%) 1,2-cyclohexenediol (19.5%). ^fBenzaldehyde (8.7%), benzyl alcohol (10.1%). ^gHomogeneous reaction in the presence of Mn(ac)₂ (0.001 mmol), conversion 38.3% after 5 h.

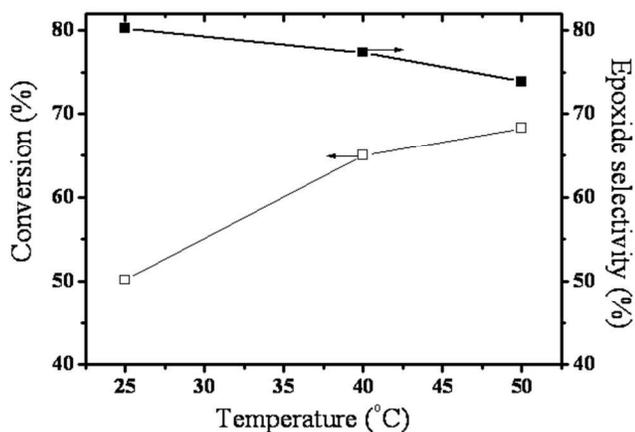
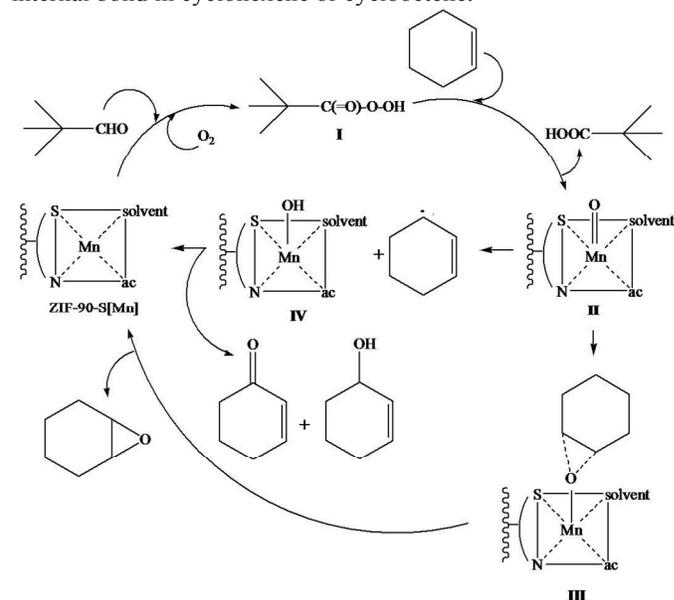


Fig. 5 Effect of temperature on the catalytic activity of ZIF-90-S[Mn] using O₂/trimethylacetaldehyde (reaction conditions: 1 mmol cyclohexene, 2 mmol trimethylacetaldehyde, 0.020 g catalyst, 5 cm³ toluene, molecular oxygen (1 atm) and 5 h).

The epoxidation of cyclohexene using molecular oxygen at atmospheric pressure with trimethylacetaldehyde as an oxidant

precursor at 40 °C produced cyclohexene oxide with good selectivity (77.4%) and conversion (65.0%) after 5 h. Fig. 5 shows the effects of the reaction temperature in cyclohexene epoxidation investigated over the range, 25–50 °C. Cyclohexene conversion increased gradually with increasing temperature, whereas the selectivity for cyclohexene oxide decreased from 82 to 74%. **3** was tested for the epoxidation of a much larger molecule, cyclooctene (size 5.5 Å), than the pore apertures of ZIF-90 (size 3.5 Å) under similar reaction conditions. At 40 °C, cyclooctene was converted to the oxide with high conversion (61.7%) and selectivity (80.2%) after 5 h, indicating that the Mn active sites are located on the external surface of **3**.

In molecular oxygen under atmospheric pressure, styrene was converted to styrene oxide with 53.8% conversion and 81.2% selectivity (Table 3). The C–C double bond attached to the benzylic ring in styrene resulted in lower reactivity than the internal bond in cyclohexene or cyclooctene.



Scheme 3 Proposed reaction mechanism for the oxidation of cyclohexene over ZIF-90-S[Mn].

The proposed reaction mechanism for the oxidation of cyclohexene is shown in Scheme 3. Mukaiyama et al. earlier reported the oxidation of alkenes using molecular oxygen in the presence of aldehyde over salen-Mn(III) complexes under homogeneous conditions.⁵³ The authors proposed that salen-Mn(III) complex reacts with molecular oxygen/aldehyde to form a highly reactive acylperoxy salen-Mn species {R₂CO₂-O-Mn(III)}, which converted alkenes to epoxide. In a similar manner, we propose that aldehyde first become converted to peracid (**I**) and subsequently generates manganese-oxo species (**II**). This metal-oxo species, **II**, reacts with cyclohexene and followed by oxo-transfer to the C=C bond in (**III**) to give epoxide. In addition, the reaction may simultaneously form allylic oxidation products via hydrogen atom transfer pathway (**IV**).⁵⁴

The catalyst stability was studied by performing a repeated epoxidation reaction under the same reaction conditions. The results are listed in Table 3 for the catalyst reused up to four times. The conversion (%) and selectivity (%) were similar irrespective of the number of cycles. No evidence for the leaching of Mn or structure deterioration of the catalyst was observed during the catalytic reaction. No traces of Mn were detected in the liquid reaction mixture by ICP-MS. The XRD

pattern of the solid catalyst after reuse was identical to that of the fresh catalyst (Fig. 1).

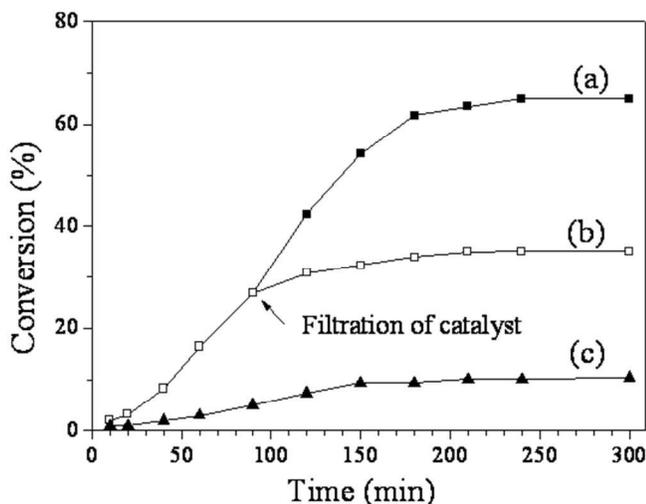


Fig. 6 Epoxidation of cyclohexene using molecular oxygen (1 atm) and trimethylacetaldehyde in toluene: (a) fresh ZIF-90-S[Mn], (b) filtered ZIF-90-S[Mn] after 90 min reaction time, and (c) without ZIF-90-S[Mn] (in the presence of O₂ (1 atm) and trimethylacetaldehyde).

Further experiments on the stability of the catalyst in cyclohexene epoxidation were carried out using a hot filtering technique, and the results are shown in Fig. 6. The catalyst was filtered off at 40 °C after 90 min to avoid re-adsorption of the potentially leached Mn onto the catalyst surface. The reaction still proceeded, but with substantially lower conversion than in the presence of the catalyst. The higher cyclohexene conversion (2.9%) in the filtrate (Fig. 6b) compared to that under the blank condition (Fig. 6c) appears to be due to the thermal reaction caused by the initially formed active radical intermediate remaining in the filtrate.⁵⁵

The homogeneous reaction carried out under the same conditions in the presence of free Mn(ac)₂ at 40 °C, confirmed that conversion of cyclohexene was much lower [38.3% conversion using 0.001 mmolMn(ac)₂] than with the ZIF-90-S-[Mn] (Table 3). The present hybrid material **3** produced comparable cyclohexene conversion but lower epoxide selectivity than that reported for the manganese(II) acetylacetonate complex binding to IRMOF-3 under identical reaction conditions.⁴⁵ In contrast, in the case of styrene, the former gave a slightly higher yield of epoxide than the latter. Considering the weak structural stability of IRMOF-3 recently reported,⁵⁶⁻⁵⁸ ZIF-90-S-[Mn] may prove to be a practical alternative for the liquid phase epoxidation reactions.

Conclusions

A thiol-functionalized ZIF-90 (ZIF-90-SH) was prepared via condensation between the free aldehyde of the ZIF-90 and the amine group of 2-mercaptoethylamine to form an imine, which was followed by the introduction of catalytically active manganese(II) acetate to furnish a hybrid material (ZIF-90-S[Mn]). The structure of the parent ZIF-90 was retained after post-synthesis functionalization. ZIF-90-SH was found to be an efficient adsorbent for the removal of Hg(II) from an aqueous solution at ambient temperature. The material exhibited an adsorption capacity of approximately 22.4 mgg⁻¹. The material was effective in the treatment of low-concentrations of Hg(II)

(10.0-0.1 mgL⁻¹) resulting in 96-98% removal of Hg(II) from aqueous solution. The new hybrid material, ZIF-90-S[Mn], showed good activity and selectivity in the epoxidation of cyclohexene, cyclooctene and styrene using molecular oxygen as the oxidant and in the presence of trimethylacetaldehyde. This solid catalyst could be recycled several times without a significant loss of activity or selectivity. The present study highlights the potential of the post-synthesis modification of MOFs to create new functionalities for the synthesis of fine chemicals and for environmental applications.

Acknowledgements

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Notes and references

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Post-synthesis functionalization of a zeolitic imidazolate structure ZIF-90: a study on removal of Hg(II) from water and epoxidation of alkenes

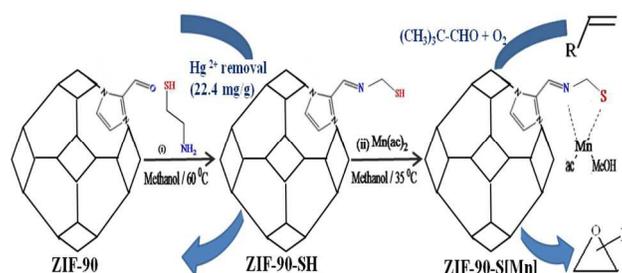
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Graphical abstract

Thiol-functionalized ZIF-90 (ZIF-90-SH) and its Mn(II)-immobilized form (ZIF-90-S[Mn]) were prepared. The former exhibited an Hg^{2+} adsorption capacity of ca. 22.4 mg g⁻¹ at room temperature and ZIF-90-S[Mn] showed good catalytic performance in the epoxidation of several important alkenes using molecular oxygen under atmospheric pressure.



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