

Mn-Metal Organic Framework as Heterogenous Catalyst for Oxidation of Alkanes and Alkenes

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Abstract

Manganese metal-organic framework (Mn-MOF) containing Mn^{2+} ions, benzenetricarboxylic acid (BTC) and *N,N*-dimethylformamid (DMF) was prepared and used as catalyst for oxidation of alkenes such as 1,1-diphenylethylene, *trans*-stilbene, cyclohexene, norbornene, styrene and cyclooctene to epoxides with 33-92% conversion and 75-100% selectivity and oxidation of alkanes such as fluorene, adamantane, ethylbenzene and diphenylmethane to alcohols or ketones with *tert*-butylhydroperoxide (TBHP) with 19-64% conversion and 80-100% selectivity. Study of the catalyst stability and reusability revealed that Mn-MOF behaves heterogeneously in the oxidation reactions.

Keywords: Mn metal organic framework; Heterogeneous catalysis; Oxidation reactions; Alkanes; Alkenes.

Introduction

The catalytic oxidation of alkanes and alkenes has been a subject of growing interest in the production of chemicals and fine chemicals. New active and selective epoxidation catalysts has been developed due to the key role of epoxides as starting materials for a wide variety of products [1-4]. On the other hand, whereas alkanes are the most abundant and least expensive chemicals for the production of valuable products, methods of selective oxidations are either rare or inefficient [5]. Transition metal complexes are successfully used to catalyze oxidation of hydrocarbons under moderate reaction conditions [6]. Among different transition metals, Mn-Schiff base complexes has been used for different oxidation type reactions [7, 8]. Interestingly, manganese compounds not only are used as active

catalysts for oxidation and epoxidation of hydrocarbons with low cost and less environmentally damaging but also are used by nature as catalytically active in a variety of metalloenzymes [9-16]. To mimic these enzymes, many manganese complexes consisting of Schiff-base ligands, porphyrins, triazamacrocyclic and phthalocyanine have been used as selective catalysts for oxidation reactions [17-21].

Microporous inorganic materials, including zeolites, aluminum phosphates, and transition-metal phosphates, are particularly important for their applications as molecular sieves, desiccants, ion exchangers, and catalysts [22-24] and thus, they have been studied in detail in the past decades. An alternative approach to obtain heterogeneous catalysts that emulate the catalytic properties of homogeneous complexes consists in the preparation of metal-organic framework materials

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(MOFs), also known as coordination polymers. MOFs have recently attracted great interest not only because of their versatile intriguing architectures and topologies but also due to their potential applications as functional materials [25-28]. In their structures, the metal ions are locally connected to the organic molecules through coordination bonds, thus resembling a spatially ordered three-dimensional array [29]. Polycarboxylic acids have been found as good candidates for the construction of novel metal-organic compounds as the carboxyl group can form C-O-M-O with four-membered rings with central metal ions [30,31]. The design and synthesis of metal-organic networks via self-assembly of metal ions and multifunctional ligands depend both on the selection of the coordination geometry of metal centers and on the various binding sites and directionality of the organic ligands [32-34]. In this study attempts has been made on using Mn-MOF as catalyst for oxidation of alkenes and alkanes.

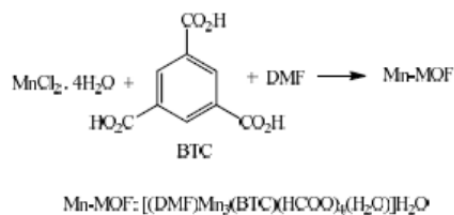
Materials and Methods

Materials and Instrumentation Details

All materials were of commercial reagent grade and used without further purification. FTIR spectra were recorded on a Bruker Tensor 27 IR spectrometer in KBr pellets over the range of 4000–400 cm^{-1} under the atmospheric conditions. X-ray powder diffraction (XRD) data were recorded on a diffractometer type, Siefert XRD 3003 PTS, using Cu K_{α} radiation ($\lambda = 1.5406 \text{ \AA}$). The amount of Mn in crystal was determined by atomic absorption spectroscopy (AAS) with a GBC spectrophotometer using flame approach. Oxidation products were analyzed by GC and GC Mass using an Agilent 6890 Series with FID detector, HP-5% phenylmethylsiloxane capillary and Agilent 5973 Network, mass selective detector, HP-5MS 6989 network GC system, respectively.

Preparation Mn-MOF

The Mn-MOF was prepared as reported [35]. A mixture of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (3.0 mmol, 0.5937 g), H_3BTC (1.0 mmol, 0.210 g), DMF (5.0 ml) and distilled water (5.0 ml) was placed in a 23 ml Teflon-lined stainless autoclave. The autoclave was sealed, heated to 120°C at a rate of a 10°C/h, under autogenous pressure for 5 days and then cooled to room temperature at a rate of 5°C/h. Colorless crystals were filtered, washed with DMF and distilled water and then dried in air. The $(\text{CH}_3)_2\text{NH}^{2+}$ and HCOO^- were generated via decomposition of DMF. Elemental analysis for $\text{C}_{15}\text{H}_{19}\text{NO}_{16}\text{Mn}_3$ (Fw: 634.13): Calcd: C, 27.85%; H, 2.94%; N, 2.16%. Found: C, 28.42%; H, 2.69%; N, 2.17%.



Scheme 1. Preparation of Mn-MOF.

Oxidation of alkenes and alkanes

Oxidation reactions were carried out in a round bottom flask equipped with a magnetic stirrer and a water-cooled condenser under atmospheric pressure. Typically, a mixture of catalyst (0.158 mmol, 100 mg) and substrate (1 mmol, in 8 ml CH_3CN) was added to the reaction flask upon slow stirring. After stirring for several minutes, TBHP (0.1 ml, 80% in di-tertiary butyl peroxide) was added and the mixture was heated at reflux for 24 h. The solid was then filtered and washed with fresh acetone. The filtrate was subjected to GC and GC mass analysis.

Results and Discussion

The Mn-MOF as a colorless crystal was prepared in high yield on the basis of the previously reported method under hydrothermal condition (Scheme 1) [35].

Catalytic activity

The epoxidation reaction of *trans*-stilbene as the representing substrate was carried out in the presence of 75 mg of Mn-MOF as catalyst. Results obtained for the effect of time on the epoxidation reaction (Fig.1) reveals 86% of *trans*-stilbene has been oxidized within 24 h, beyond which no further oxidation occurs during the next 12 h.

As indicated in Fig. 2, changing the amount of catalyst from 35 mg to 100 mg increases the conversion from 75% to 92%. Therefore, other epoxidation

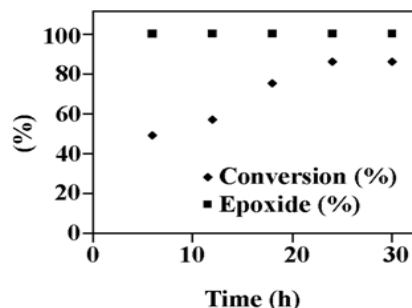
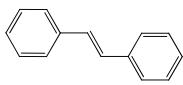
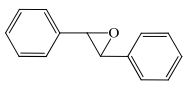
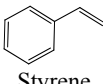
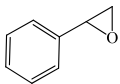
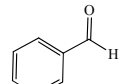
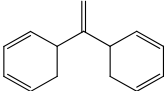
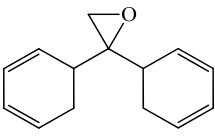
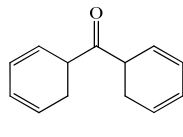




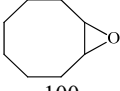

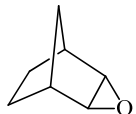


Figure 1. Effect of time on oxidation of *trans*-stilbene with TBHP in the presence of Mn-MOF in CH_3CN .

Table 1. Results of the oxidation of organic hydrocarbons with TBHP in the persence of Mn-MOF

Entry	Substrate	Conversion (%)	Major product (%)	Minor product (%)	Time (h)
1	 <i>trans</i> -Stilbene	92	 100	-	24
2	 Styrene	85	 54	 46	24
3	 1,1-Diphenylethylene	33	 84	 16 25	24
4	 Cyclohexene	100	 75	 25	24
5	 Cyclooctene	55	 100	-	24
6	 Norbornene	96	 100	-	24

Reaction conditons: substrate (100 mg), catalyst (150 mg), TBHP (80%, 0.1 ml), solvent (8 ml).

reactions were carried out within the optimal conditions (24 h and 100 mg of catalyst).

The epoxidation results of *trans*-stilbene, styrene, diphenylethylene, cyclohexene, cyclooctene and norbornene with Mn-MOF in acetonitrile as solvent and

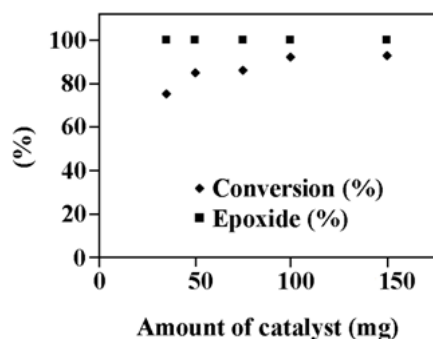
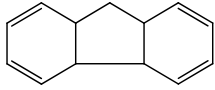
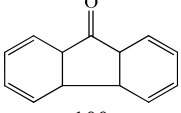
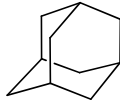
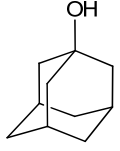
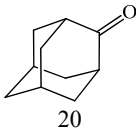
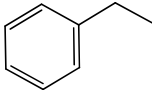
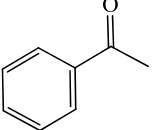
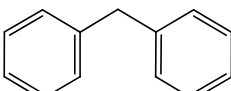
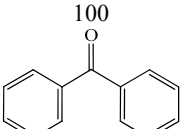


Figure 2. Effect of the amount of catalyst on oxidation of *trans*-stilbene with TBHP in the presence of Mn-MOF in CH₃CN.

TBHP as oxidant are given in Table 1(entries 1-6). Selective epoxidation of norbornene, *trans*-stilbene and cyclooctene along with styrene which has undergone competitive oxidation to styrene epoxide and benzaldehyde are notable. On the other hand, whereas 1,1-diphenylethylene has totally proceeded to diphenylketone, oxidation of cyclohexene has exceptionally occurred via allylic C-H, affording 2-cyclohexene-1-ol (25%) and 2-cyclohexene-1-one (75%). Observation of no catalyst active species desorption under oxidation conditions due to the stability of the catalysis system is promising. The stability of the Mn-MOF was also studied by recycling of the easily recovered catalyst and redetermination of the metal content using atomic absorption spectroscopy. Compared to the initial catalyst manganese content which was 23.84%, it was found to be 22.87% in the used catalyst.

The oxidation results of flourene, adamantane, ethylbenzene, and diphenylmethane are given in Table

Table 2. Results of the oxidation of organic hydrocarbons with TBHP in the persence of Mn-MOF

Entry	Substrate	Conversion (%)	Major product (%)	Minor product (%)	Time (h)
1	 Fluorene	64	 100	-	72
2	 Adamantane	53	 80	 20	24
3	 Ethylbenzene	34	 100	-	24
4	 Diphenylmethane	19	 100	-	24

Reaction conditons: substra (100 mg), catalyst (150 mg), TBHP (80%, 0.1 ml), solvent (8 ml).

2. Whereas Mn-MOF catalyzed oxidation of fluorene, ethylbenzene and diphenylmethane to the corresponding ketones with excellent selectivities (entries 1, 3, 4, Table 2), adamantane has undergone oxidation to a mixture of the corresponding 1-ol and 2-one with the ratio of 4 to 1 (entry 2, Table 2). With the exception of adamantane which is usually used both as substrate and mechanistic probe (vide infra), obtaining ketones with excellent selectivities is notable.

The FT-IR spectra of Mn-MOF before and after reaction are depicted in Fig. 3a-b, respectively. As is observed, the broad band due to symmetric stretching vibration of water appears at 3397 cm^{-1} [36-37] and the bands displaying at 1664 to 1500 and 1439 to 1337 cm^{-1}

¹ correspond to the asymmetric and symmetric stretching vibrations of the bound carboxylic groups (CO_2M) [36-39]. In addition, the bands appearing at 864 cm^{-1} and 772 cm^{-1} are related to the stretching and out-of-plane deformation vibrations of the of benzene C-C and C-H groups, respectively. The absence of the absorption bands in the region of 1680 to 1800 cm^{-1} is in accord with complete BTC ligand deprotonation[38]. Finally, the group bands displaying at 2866 to 2971 cm^{-1} are due to the asymmetric and symmetric stretching vibrations of H_2N^+ groups [35]. Particularly significant is the similarity of the FTIR spectra of the used catalyst (Fig. 3b) with that of the fresh catalyst (Fig. 3a).

The XRD patterns of the fresh and used catalysts

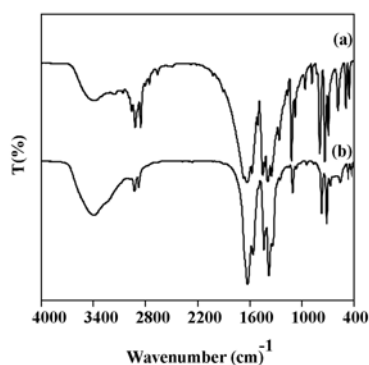


Figure 3. FTIR spectra of Mn-MOF (a) before and (b) after using as catalyst.

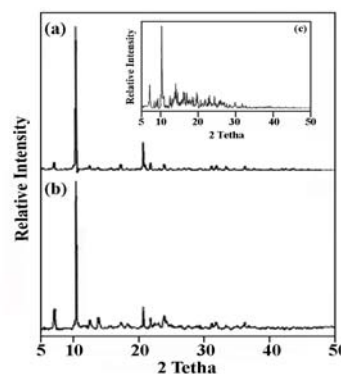
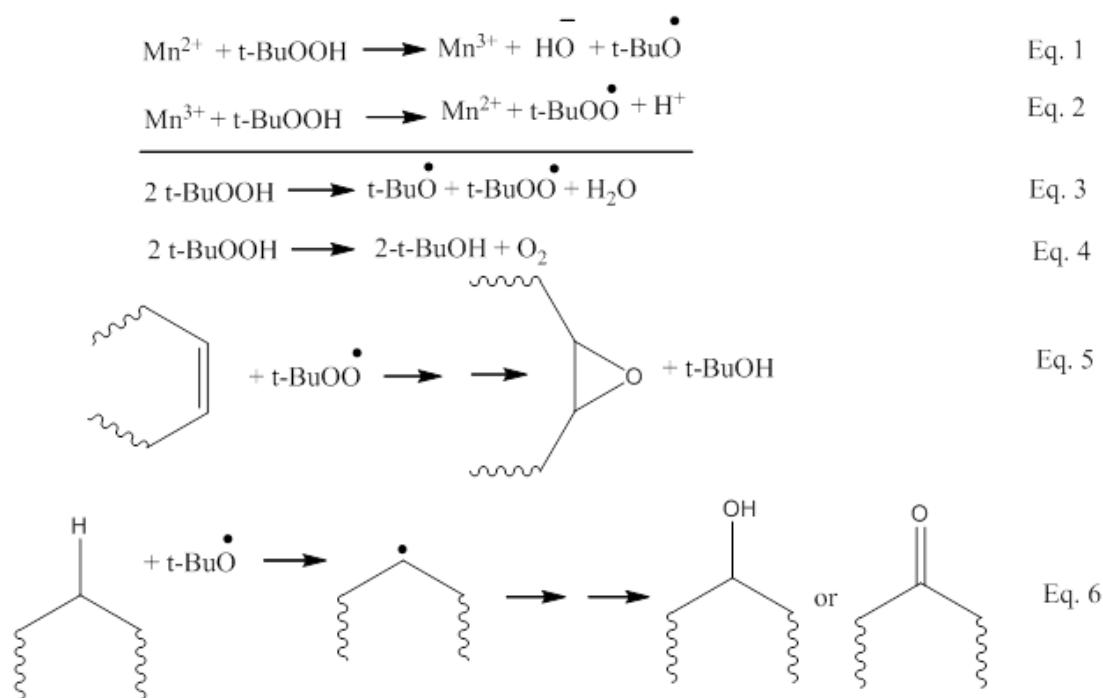


Figure 4. Powder XRD patterns of Mn-MOF (a) fresh, (b) reused and (c) simulated.



Scheme 2. Suggested mechanism for oxidation of alkenes and alkanes.

indicated in Fig. 4a,b respectively. The simulated XRD pattern of Mn-MOF for comparison are also shown in Figure 4c. The obtained results clearly reveal the survival of the Mn-MOF crystalline structure after using the catalyst in the oxidation reactions. Notably, no change has occurred in the patterns and observation of increased noise seems to be due to partial pore blocking occurred during the reaction [40].

Based on our knowledge comparing this work with those reported before, the stability, selectivity and heterogeneous character of the prepared catalyst is considerable.

Mechanism of catalytic activity

Total suppression of *trans*-stilbene epoxidation in the presence of an equimolar of diphenylamine as well as the concomitant formation of adamantane-1-ol and 2-one [41] strongly support the operation of a radical pathway. Therefore, the implication of t-BuO and t-BuOO radical intermediates obtained from one-electron oxidation-reduction processes is conceivable (Eq. 1, 2 and 3, Scheme 2). Therefore, epoxidations and oxidations may have proceeded from addition of t-BuOO radical to the alkene double bonds (Eq. 5, Scheme 2), or H-abstraction to t-BuO radical (Eq. 6, Scheme 2), respectively.

In summary, In this study, Mn-MOF has been used as catalyst for oxidation of cyclic alkenes and alkanes with

TBHP in CH₃CN. It was found that Mn-MOF successfully catalyzes the epoxidation of alkenes such as *trans*-stilbene, cyclohexene, norbornene, styrene, cyclooctene and 1,1-diphenylethylene and the oxidation of some alkanes such as fluorene, adamantane, ethylbenzene, diphenylmethane. The observation of such catalytic behavior with no significant amount of catalyst desorption or decomposition during the course of the reactions proves the heterogeneous nature of catalyst.

Acknowledgment

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