



## Short Communication

## Highly active dimeric Mn(salen) catalysts entrapped within nanocages of periodic mesoporous organosilica for epoxidation of alkenes

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## ABSTRACT

A couple of robust and reusable diamine-bridged dimeric Mn(salen) complexes were prepared by the encapsulation of homogeneous dimeric Mn(salen) complexes into nanocages of three-dimensionally (3D) periodic mesoporous organosilica (PMO) support followed by the silylation of the support with organosilane. The materials exhibited 3D periodic mesostructure with body-centered *Im3m* symmetry, and the confined Mn(salen) complexes maintained their original structure. As-prepared heterogeneous dimeric Mn(salen) complexes were successfully applied in the epoxidation of three alkenes (*i.e.* styrene, cyclohexene, and 1-phenylcyclohexene) by using NaClO as the oxygen donor and CH<sub>2</sub>Cl<sub>2</sub> as a solvent, and the reusability of the materials was evaluated through three times' catalytic runs.

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## 1. Introduction

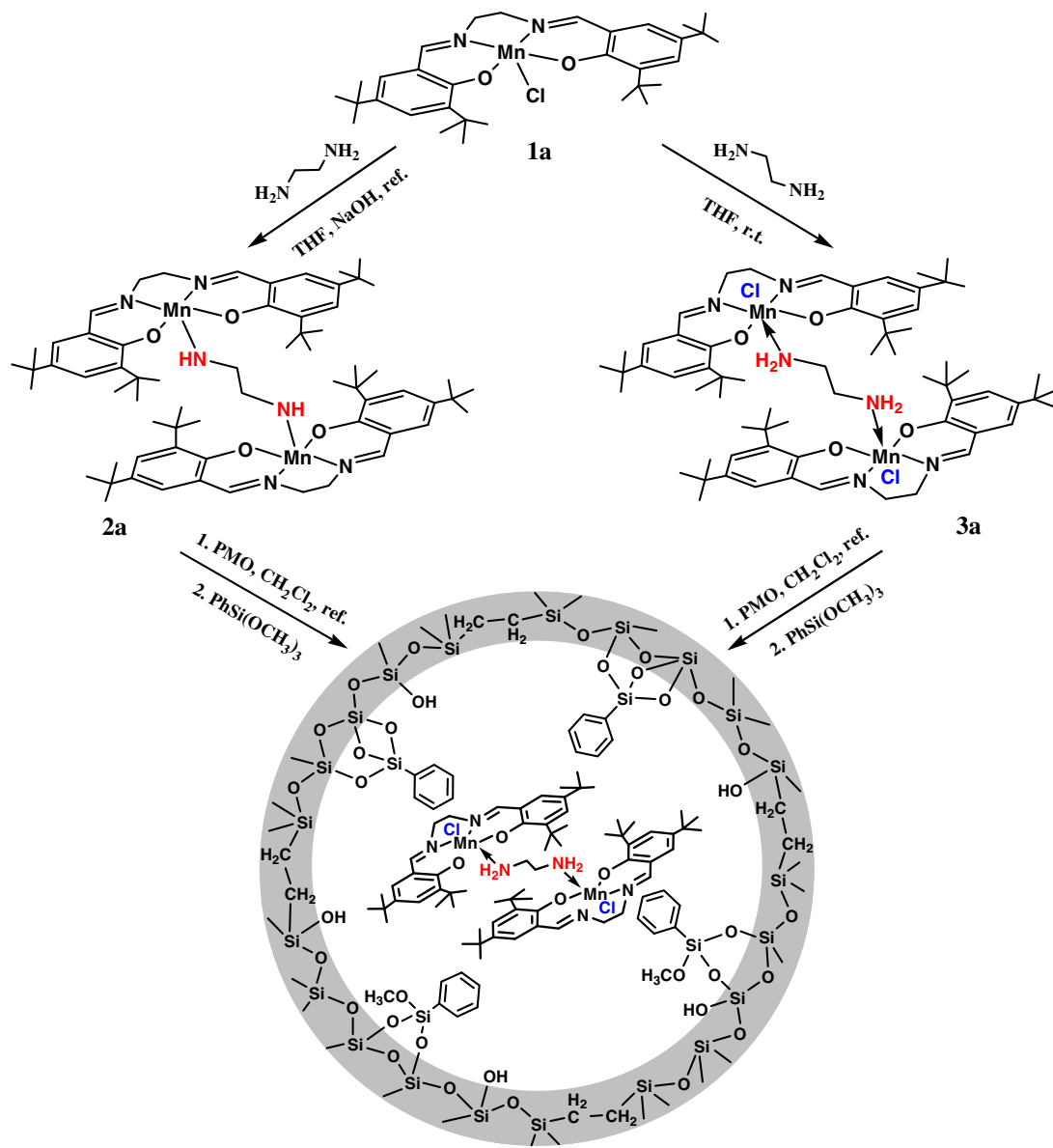
Epoxides are an important class of industrial chemicals that have been used as chemical intermediates, and catalytic epoxidation of alkenes to form epoxides affords an interesting production technology [1]. As one of the most effective processes, salen–metal complex-catalyzed alkene epoxidation has received especial attentions [2–12]. Moreover, the trend to develop reusable salen–metal complexes with high efficiency and catalytic stability is increasing from the environmental concerns together with economic considerations. Accordingly, methodologies for the heterogenization of homogeneous salen–metal complexes have emerged [13]. Among them, heterogenization of salen–metal complexes into/onto inorganic or inorganic–organic hybrid supports is one of the promising strategies. For these supported salen–metal complexes, the host–guest interaction can be mechanical, physical, or chemical [3,13].

In search for efficient and recyclable epoxidation catalysts, we herein demonstrated a couple of robust and reusable diamine-bridged dimeric manganese–salen complexes for the first time. The preparation procedure included the encapsulation of homogeneous dimeric Mn(salen) complexes (**2a** or **3a**, obtained by axial coordination of monomeric Mn(salen) complex (**1a**) with diamine in the presence and absence of NaOH) into the nanocages of SBA-16-like 3D PMO

support firstly, and then the free surface silanol groups of PMO support were silylated with phenyltrimethoxysilane (phTMS), as illustrated in Scheme 1. After the above two steps, the dimeric Mn(salen) complexes were entrapped and imprisoned within the cages of PMO support due to the relative dimension of guest and host. Unlike most of the immobilized salen–metal complex systems, no structural modification of the complexes would be required for as-prepared **2a**/PMO-ph and **3a**/PMO-ph materials and thereby the trapped dimeric Mn(salen) complex (**2a** or **3a**) may be kept as that of its free form [8]. Furthermore, the complexes would be accessible throughout the multidirectional pore systems since the reactions catalyzed by **2a**/PMO-ph or **3a**/PMO-ph may occur within its 3D cage-like pores. Compared with zeolite support, PMO with a large pore diameter and high periodicity is expected to provide sufficient space to accommodate large dimeric Mn(salen) complexes, which is another key factor to ensure excellent catalytic activity of as-prepared supported Mn(salen) complexes. The purpose of selecting dimeric Mn(salen) complexes as the active components is to increase the heterogeneous catalytic activity and stability of monomeric Mn(salen) complexes towards the alkene epoxidation reactions. On the one hand, the catalytic activity of Mn(salen) complexes is expected to be enhanced owing to the increase of the local concentration of the active sites; meanwhile, diamine group that is used to bridge two monomeric Mn(salen) complexes, is a good electron-donor that can facilitate the electron transfer between the Mn(salen) complexes and alkenes. On the other hand, the stability of the immobilized dimeric Mn(salen) complexes is expected to be improved since the solubility

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**Scheme 1.** Pathway of the synthesis of diamine-bridged dimeric Mn(Salen) complexes (**2a** and **3a**) and their corresponding heterogeneous analogues (**3a**/PMO-ph as the representative).

of the dimeric complexes is considerably low in contrast with the corresponding monomers [8]. Through alkene epoxidations the heterogeneous catalytic activity and stability were evaluated by using NaClO as the oxygen donor and  $\text{CH}_2\text{Cl}_2$  as a solvent.

## 2. Experimental

### 2.1. Catalyst preparation

Procedure of the preparation of heterogeneous Mn(salen) complexes was described below. SBA-16-like PMO support and **1a** were prepared according to the literature methods [14–16]. **2a** was prepared by refluxing the mixture of **1a** (2.0 mmol) and diamine (1.0 mmol) in THF (5 mL) for 6 h in the presence of NaOH (2.2 mmol). **3a** was prepared by stirring the mixture of **1a** (2.0 mmol) and diamine (1.0 mmol) in THF (5 mL) at room temperature for 6 h in the absence of NaOH (Scheme 1). Afterwards, PMO support (1.0 g) was dispersed into **1a**, **2a**, or **3a** (0.15 g)-containing dichloromethane (5 mL). After the mixture was stirred at 323 K for 24 h, dichloromethane was removed by evaporation. The resultant solid was introduced into a

mixture of toluene (1.5 mL), triethylamine (1.2 mL), and  $\text{pHMS}$  (5.0 mmol) and then the mixture was refluxed for 24 h. Subsequently, the product was isolated by filtration, washed with toluene and dichloromethane at least for three times, and dried in vacuum. The products were denoted as **1a**, **2a**, or **3a**/POM-ph, and loading of **1a**, **2a**, and **3a** (wt.%) in the Mn(salen)/POM-ph materials was 1.2%, 2.4%, and 2.0%, respectively, estimated by a Leeman Plasma Spec (I) ICP-AES.

### 2.2. Catalyst characterization

FT-IR spectra were recorded on a Nicolet Magna 560 IR spectrophotometer with  $n$  of scans of 16, frequency interval of  $2\text{ cm}^{-1}$ , and resolution of  $0.4\text{ cm}^{-1}$ , and the samples were firstly mixed with KBr powder and then were produced into pellets. Low-angle XRD patterns were obtained on a D/max-2200 VPC diffractometer using  $\text{CuK}\alpha$  radiation. Nitrogen porosimetry measurement was performed on a Micromeritics ASAP 2020M surface area and porosity analyzer after the samples were outgassed under vacuum at  $90\text{ }^\circ\text{C}$  for 1 h and  $180\text{ }^\circ\text{C}$  for 6 h. TEM images were obtained on a JEOL JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV.

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