



Epoxidation of alkenes catalyzed by highly ordered mesoporous manganese–salen-based hybrid catalysts



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ABSTRACT

A series of manganese–salen-based hybrid catalysts, Mn(salen)/C₃N₂–Schiff–SBA-15 and Mn(salen)/C₄N₂–Schiff–SBA-15, were demonstrated for the first time by a multistep grafting method. As-prepared hybrid catalysts exhibited well-defined mesostructure including highly ordered 2D hexagonal *p6mm* pore geometry, large BET surface area (268–293 m² g⁻¹), uniform pore size (5.2–6.4 nm) as well as high pore volume (0.35–0.41 cm³ g⁻¹); meanwhile, the structure of the starting manganese–salen complexes and other functionalities (Schiff ligand and C₃N₂ or C₄N₂ unit) remained intact in the hybrid catalysts. These hybrid catalysts were subsequently utilized as efficient, selective and reusable catalysts in epoxidation of alkenes including styrene, cyclohexene and 1-phenylcyclohexene by using NaOCl as the oxidant, and the contribution of imidazole or piperazine and Schiff base to the overall catalytic activity of the hybrid catalysts were evaluated and explained.

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1. Introduction

Epoxides are an important class of industrial chemicals, and epoxidation of alkenes to epoxides catalyzed by metal–salen complexes affords an interesting production technology and thus receives extensive attentions [1–3]. In the catalytic point of view, metal–salen complexes are highly effective in the epoxidation reactions in the presence of environmentally clean oxidants such as molecular oxygen and NaOCl. However, metal–salen complex-catalyzed reactions generally proceed in homogeneous systems, and the major drawback of homogeneous catalysis is the need for separation and recovery of the metal–salen complexes from the reaction mixture at the end of the process [4–14]. From the environmental concerns together with economic considerations, the development of sustainable metal–salen complex-catalyzed heterogeneous processes is of great interest. It has been proved that the heterogenization of homogeneous metal–salen complexes onto/in various solid supports including zeolites [15], silica materials [16–18], carbon materials [19,20], organosilica materials [21,22], layered compounds [23–25] as well as polymer [26] *via* dative, covalent, encapsulation, adsorption or electrostatic binding is one of the efficient methodologies to prepare the heterogeneous metal–salen catalysts [27–35]. Moreover, considering the catalytic stability of the immobilized metal–salen catalysts, chemically

anchored metal–salen complexes are the promising candidates towards the epoxidation reactions. Previously we have reported mesoporous propylthiol group-functionalized silica supported manganese(III)–salen complexes (Mn(salen)/*pr*-S-SiO₂), in which propylthiol group-functionalized silica support interacts with manganese(III)–salen complexes *via* C–S covalent bond. The prepared Mn(salen)/*pr*-S-SiO₂ exhibited excellent catalytic oxidation activity and stability towards the epoxidation of styrene by using aqueous NaOCl as the oxygen source [36]. More recently, Burri's group has prepared SBA-Fe (acetylacetonate:salen) and SBA-VO (acetylacetonate:salen) heterogeneous catalysts, and the catalysts have been proved to be highly active and selective towards the cleavage of aliphatic C=C bond of styrene to benzaldehyde [37,38].

In the search for novel heterogeneous metal–salen catalysts for the synthesis of epoxides, herein, a series of recoverable and reusable manganese–salen-based hybrid catalysts, Mn(salen)/C₃N₂–Schiff–SBA-15 and Mn(salen)/C₄N₂–Schiff–SBA-15 with highly ordered mesostructure, were demonstrated for the first time by a multistep grafting method. In these hybrid catalysts, homogeneous Mn(salen) complexes linked with imidazole (C₃N₂) or piperazine (C₄N₂)–Schiff base-functionalized SBA-15 silica support *via* C–N covalent bond formed due to the interaction of benzyl chloride group in the Mn(salen) ligands with nitrogen atoms of C₃N₂ or C₄N₂ unit in the functionalized SBA-15 silica supports (Scheme 2). Purpose of current design is further improvement of the catalytic oxidation activity and stability of heterogeneous manganese–salen complexes. On the one hand, Schiff base ligands are composed of rich electron-donating groups, and Schiff base complex-catalyzed

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oxidation of organic compounds has showed considerably high catalytic activity and selectivity [39]. Therefore, the oxidation of hydrocarbons using Schiff base complexes has been a field of academic and industrial interest. For examples, silica-immobilized oxo-vanadium(IV) tridentate Schiff base complex prepared via covalent attachment can effectively and smoothly oxidize sulfides to the corresponding sulfones using aq. *tert*-butyl hydroperoxide (TBHP) as a oxidant [40]. Amine-functionalized mesoporous silica supported copper(II)- or nickel(II)-Schiff base complex prepared via a multistep grafting method exhibited highly activity towards the selective epoxidation of olefins to their corresponding epoxides in the presence of TBHP [41]. Imidazole and piperazine also possess electron-donating ability. The introduction of both Schiff base and imidazole/piperazine units in the manganese-salen-based hybrid catalysts can significantly facilitate the electron transfer rate of manganese-salen complexes, accordingly, the overall oxidation catalytic activity of the Mn(salen)/C₃N₂-Schiff-SBA-15 and Mn(salen)/C₄N₂-Schiff-SBA-15 is expected to be enhanced compared with pure SBA-15 silica supported manganese-salen complexes. Additionally, the catalytic stability of Mn(salen)/C₃N₂-Schiff-SBA-15 and Mn(salen)/C₄N₂-Schiff-SBA-15 is expected to be enhanced because Mn(salen) complexes were chemically anchored on the functionalized SBA-15 silica support. On the other hand, as-prepared manganese-salen-based hybrid catalysts exhibited well-defined porosity including highly ordered 2D hexagonal *p6mm* pore geometry, large surface area, large pore diameter and high pore volume, allowing more facile diffusion of the reactants and products. This unique surface physicochemical property plays an important role to improve the catalytic activity of manganese-salen complexes since the performance of the heterogeneous catalysts is also determined to a great extent by their textural properties. Accordingly, as-designed manganese-salen-based hybrid catalysts are expected to be promising candidates for the synthesis of epoxides by the combination of the enhanced electron transfer rate of manganese-salen complexes and the excellent textural properties. Moreover, in order to further adjust the catalytic activity of as-prepared manganese-salen-based hybrid catalyst towards epoxidation of alkenes, two starting manganese-salen complexes with different substituents (i.e. cyclohexyl group and ethyl group) in the diimine bridges were chosen as the precursors (Scheme 2).

The composition, structure, morphology, and textural properties of as-prepared hybrid catalysts were characterized by spectroscopy methods, X-ray diffraction analysis, transmission electron microscopy and nitrogen physisorption measurement. Subsequently, their catalytic performances were tested by epoxidation of various alkenes including styrene, cyclohexene and 1-phenylcyclohexene by using NaOCl as the oxidant and 4-phenylpyridine N-oxide (PPNO) as the axial ligand, meanwhile, the contribution of imidazole/piperazine and Schiff base to the overall catalytic oxidation activity of the hybrid catalysts were evaluated and explained. Finally, the recovery and reuse of the heterogeneous Mn(salen) complexes were evaluated.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (abbreviated as TEOS, 98.0%), 3-aminopropyl-trimethoxysilane (abbreviated as APS, 98.0%), 4-phenylpyridine N-oxide (abbreviated as PPNO) and Pluronic P123 (EO₂₀PO₇₀EO₂₀, where EO = -CH₂CH₂O-, PO = -CH₂(CH₃)CHO-) were purchased from Aldrich and used without further purification. Styrene (99.0%) was purchased from Tianjin Guangfu Fine Chemical Research Institute (China). All other chemicals were

analytical grade and were purchased from Beijing Fine Chemical Co. (China).

2.2. Catalyst preparation

SBA-15 silica support. SBA-15 silica support was prepared following the literature method [42]. Briefly, P123 (4 g) was dissolved in an aqueous HCl solution (2 mol L⁻¹, 120 mL) and then 30 mL of water under stirring at ambient temperature for 1 h. Subsequently, TEOS (8.5 g) was added into the above P123 solution under stirring at 313 K for 20 h. The resulting mixture was subjected to hydrothermal treatment at 373 K for 24 h at a heat rate of 2 K/min. The separated white powder was washed with deionized water for three times, and then it was dried at room temperature. Finally, the product was calcined at 773 K in air for 6 h to remove P123. In order to evaluate the other mesoporous manganese-salen-based hybrid catalysts on their catalytic activity, two other supports, periodic mesoporous organosilica (PMO) and 3D interconnected silica (3D_{int}-SiO₂), were also prepared according to the literature methods [42].

Amine-functionalized SBA-15 silica support (NH₂-SBA-15). APS (2 mol) was dispersed into a suspension including ethanol (50 mL) and SBA-15 silica (1 g). The mixture was stirred vigorously at room temperature for 24 h, and then the product was recovered by centrifugation after washing with ethanol and diethyl ether, respectively [24].

Imine-functionalized SBA-15 (Schiff-SBA-15). NH₂-SBA-15 silica (1 g, activated under vacuum at 373 K for 1 h) was dispersed into the mixture of 3-*tert*-butyl-2-hydroxybenzaldehyde (2 mol) and ethanol (50 mL). After the suspension was stirred for 12 h at room temperature, the solid product was obtained via filtration followed by ethanol washing and air drying at 373 K [25].

C_nN₂-Schiff-SBA-15. Imidazole or piperazine (2 mmol) was added into a toluene solution (10 mL), and then the freshly activated Schiff-SBA-15 (1 g) was added into the above solution. The mixture was refluxed at 386 K for 24 h, and then it was centrifuged, washed with ethanol and dried at 373 K, successively.

Salen ligand a [N-(3-*tert*-butyl-5-chloromethyl-salicylidine)-N-(3-*tert*-butyl-5-chloromethyl-salicylidine)-1,2-cyclohexanediamine] and **salen ligand b** [N-(3-*tert*-butyl-5-chloromethyl-1-salicylidine)-N-(3-*tert*-butyl-5-chloromethyl-salicylidine)-1,2-ethylenediamine]. 3-*tert*-butyl-5-(chloromethyl)-2-hydroxybenzaldehyde (4 mmol) was added into a absolute ethanol solution (10 mL) containing (2 mmol) of diamine derivatives (cyclohexane-1,2-diamine for salen ligand **a** and ethane-1,2-diamine for salen ligand **b**). The resulting mixture was refluxed (353 K) for 3 h, and then it was cooled to room temperature. Subsequently, deionized water (3 mL) was added dropwise to the cooled bright yellow solution. The mixture was kept at 277 K for 48 h, and the formed yellow crystalline solid was collected by filtration. Then it was washed with a small amount of ethanol (95%). The above procedure is presented in Scheme 1.

Mn(salen)/C_nN₂-Schiff-SBA-15 (n = 3, 4). C₃N₂-Schiff-SBA-15 or C₄N₂-Schiff-SBA-15 (1.0 g) was added to a toluene solution (10 mL) containing salen ligand **a** or **b** (0.3 mmol) under refluxing (386 K) for 24 h. The product was collected by filtration, washed with ethanol and dichloromethane for three times and dried at 323 K under vacuum for 12 h. The obtained C_nN₂-Schiff-SBA-15 supported salen ligand **a** or **b** was dispersed into an ethanol solution containing Mn(OAc)₂·4H₂O (0.294 g), and the resulting mixture was refluxed at 363 K for 5 h, followed by another 3 h after the addition of LiCl (0.076 g). The resulting solid product was washed with water and ethanol, and the separated light-brown powder was dried in a vacuum at 373 K. The final product was denoted as **a(x)/C₃N₂-Schiff-SBA-15**, **b(x)/C₃N₂-Schiff-SBA-15**, **a(x)/C₄N₂-Schiff-SBA-15**, and **b(x)/C₄N₂-Schiff-SBA-15**, respectively,

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