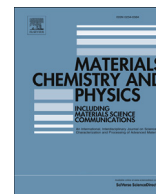




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Covalent immobilization of the Jacobsen catalyst on mesoporous phenolic polymer: A highly enantioselective and stable asymmetric epoxidation catalyst

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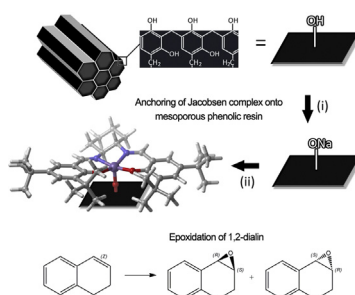
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HIGHLIGHTS

- Synthesis of mesoporous phenolic resin with high specific surface area and large pores.
- Covalent immobilization of a manganese-salen complex on mesoporous polymer.
- Enantioselective epoxidation of dialin with a heterogeneous catalyst.
- Demonstration of leaching resistance in organic solvent.

GRAPHICAL ABSTRACT



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ABSTRACT

The Jacobsen catalyst, *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminomanganese (III) chloride is covalently immobilized on mesoporous phenolic resin through a direct and simple procedure. The immobilization is evident from nitrogen sorption and quantitative XRF measurements. A complex loading of 0.09 mmol g⁻¹ is obtained, corresponding to well dispersed Mn-complexes on the surface of the mesoporous phenolic resin. This novel catalytic system shows good catalytic activity and excellent enantioselectivity in the asymmetric epoxidation of 1,2-dialin. The heterogenized Jacobsen catalyst is demonstrated to be a re-usable and non-leaching catalytic system.

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1. Introduction

Epoxides are versatile intermediates in organic chemistry. Their inherent polarity and the strain in the three-membered ring makes them interesting compounds for regioselective ring opening

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reactions, followed by the formation of 1,2-difunctional products [1–3]. In particular, optically pure epoxides with two vicinal chiral centers are often used as intermediate in the synthesis of biologically and pharmaceutically active compounds [4]. Today, the synthesis of chiral epoxides generally occurs by oxidation of olefins. In this field, the asymmetric epoxidation of unsubstituted alkenes is not facile since no substituents are present to control the orientation of the substrate. The Jacobsen catalyst, a manganese (III) *salen* complex, has proven to be a very efficient catalyst for asymmetric alkene epoxidation reactions [5]. As shown in Fig. 1 (Left), these *salen*-type complexes have two chiral sp^3 hybridized carbon atoms (*) in the vicinity of the metal center. The presence of these two stereogenic centers enables excellent stereochemical control in the epoxidation step. Furthermore, these complexes possess bulky *t*-butyl groups on the aromatic rings, acting as substrate directing agents (Fig. 1). The Jacobsen catalyst can react with a variety of terminal oxidants, such as hydrogen peroxide, sodium hypochlorite and iodossyl arenes, forming activated oxo-manganese (V) species that are able to epoxidize contacting alkene substrates [6].

Fig. 1 (Right) shows the activated Jacobsen catalyst. Due to sterical hindrance of the bulky *t*-butyl groups, the olefin substrates are forced to approach the activated manganese center via the dissymmetric diimine bridge (pathways *a*, *b* and *b'*) [7,8].

The major drawback of these catalysts, however, is the deactivation process in homogeneous phase due to the formation of inactive dimeric μ -oxo-manganese (IV) species [9–11]. In recent years, heterogenization through immobilization of these homogeneous *salen*-type catalysts on mesoporous supports has become an object of intensive research. Due to local site isolation of the complexes on a solid matrix, dimerisation can be prevented. Furthermore, the possibility of simple recyclability after the catalytic run makes these expensive complexes more economically attractive. The majority of the reports on the heterogenization of Mn (III) *salen* catalysts have mostly been centered on encapsulation, adsorption or covalent attachment to porous inorganic supports, such as zeolites, MCM-41, Al-MCM-41, mesoporous silicagel, SBA-15 and clays [1,12–19]. These strategies have proven to be efficient, yet for covalent immobilization the original structure of the manganese complex is modified or multiple synthetic steps and structural changes to the parent catalyst structure and support are required. Intensive research on the heterogenization of *salen*-type and other metal complexes has been performed by De Vos et al., being particularly successful in the field of zeolite encapsulation and silica grafting [20–22]. Various *metallo-salen* complexes and analogues have been anchored successfully on hybrid porous materials such as ordered mesoporous organosilicas (PMOs) and metal organic frameworks (MOFs) [23]. Various attempts to produce polymer-supported Jacobsen catalysts have been reported, e.g. through attachment via the aromatic rings, by binding pre-formed Mn-complexes to a pyridine-containing polystyrene-based resin or by physical entrapment of the complex within a suitable polymer

matrix [24–28]. Silva et al. published the immobilization of the Jacobsen catalyst through a direct axial coordination of the metal center onto the phenolate groups of a modified, commercial, activated carbon [29]. This immobilization procedure involves a direct and simple reflux procedure. The newly developed catalysts showed high activity in the asymmetric epoxidation of styrene and α -methylstyrene, using PhIO and *m*-CPBA as oxidants. However, the obtained *ee* values were rather moderate [30]. Also, prior to the immobilization of the manganese complex on activated carbon, the carbon surface has to be pre-treated by an oxidation step (mostly by H_2O_2 treatment or with an air flow) in order to generate sufficient surface phenolic hydroxyl functions as anchoring points [29]. When the procedure was applied on carbon xerogels, the surface pre-treatment was performed under 5% O_2 [31].

In this study, mesoporous phenolic resins are introduced as a novel support for the manganese (III) *salen* complex. These phenolic resins are an advanced class of mesoporous materials combining a high porosity with the organic properties of the corresponding polymer. Moreover, this new generation of mesoporous materials has shown to be highly stable, both thermally and mechanically [32,33]. The mesoporous phenolic resins contain an abundance of phenolic hydroxyl groups in their framework. Consequently, the pre-oxidation is not required for these materials, providing a time efficient synthesis pathway. This newly developed catalyst is evaluated for its catalytic performance in the asymmetric epoxidation of dialin (1,2-dihydronaphthalene). The results are compared to the catalytic activity of the homogeneous Jacobsen catalyst system. To evaluate the recyclability and the resistance to leaching, the heterogeneous catalyst was used in three consecutive epoxidation reactions.

2. Experimental

2.1. Chemicals

Resorcinol, Formalin (36%), Pluronic F127, Jacobsen catalyst (N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminomanganese (III) chloride), 1,2-dihydronaphthalene and sodium hypochlorite solution (10%) were purchased from Sigma Aldrich. Suprapur Nitric acid 65% was purchased from Merck Chemicals. All chemicals were used as received.

2.2. Synthesis of mesoporous phenolic resin

In a typical synthesis, resorcinol (2.2 g) and Pluronic F127 (2.2 g) were dissolved in ethanol (9.0 mL) containing HNO_3 (3 M, 9 mL) during 15 min at room temperature. Subsequently, 2.6 g of aqueous formaldehyde solution (36 wt %) was added dropwise to the above solution, under continuous stirring. After an additional 15 min of stirring, the resulting clear solution was poured and dried on a dish during 6 h to evaporate the ethanol. The sample was then collected

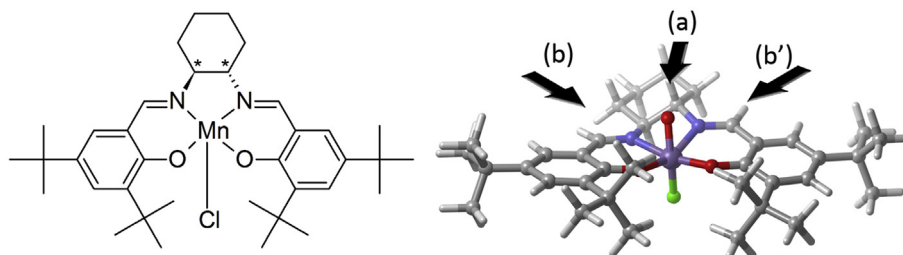


Fig. 1. (Left) Structure of the Jacobsen catalyst, N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminomanganese (III) chloride. The chiral carbon atoms are denoted with an asterisk. (Right) Spatial structure of the activated Jacobsen catalyst. The arrows indicate the possible approaches of the olefin substrates to the active site of the catalyst.

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