

Chiral Salen Manganese Complex Immobilized on SBA-15: A New Heterogenized Enantioselective Catalyst for the Epoxidation of Alkenes

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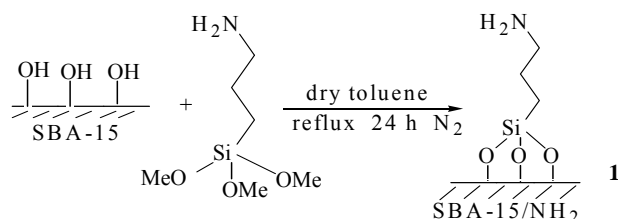
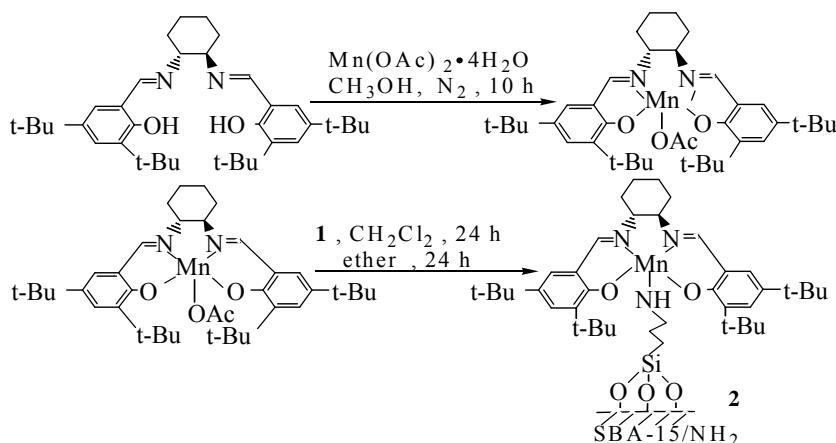
Abstract: Jacobsen's catalyst was immobilized onto SBA-15 by multi-step grafting, and this heterogenized catalyst exhibited comparable catalytic performance with the corresponding homogeneous counterpart for the epoxidation of alkenes, and the catalyst could be recycled effectively several times.

Keywords: SBA-15, chiral salen Mn(III) complex, alkenes, asymmetric epoxidation.

The use of chiral catalysts has become a powerful methodology in modern synthetic organic chemistry¹. More recently, Jacobsen and co-workers expanded the scope of the catalytic asymmetric epoxidation to the unfunctionalized alkenes with high stereo controlling by using chiral (salen)Mn complexes².

The classical salen-Mn(III) catalysts showed high activities and enantioselectivities for the reaction, however, the separation and recycling of the catalyst are still major problems. Heterogeneous systems have tremendous advantages over homogeneous catalytic system³. One of the most attractive advantages is the easy separation of the product from the catalyst without tedious experimental work-up. These encouraged some authors to develop supported salen-Mn(III) catalysts. Ogunwumi and Bein⁴ showed that manganese(III)-salen complexes could be encapsulated in the pores of zeolite Y by appropriate synthetic methods. The ion-exchange of manganese(III) complexes into zeolite Y⁵ or MCM-41⁶ has also been reported. It seems that the adjustment of support material is to be the basis for the further development of the catalyst⁷. SBA-15, developed by Stucky *et al.*⁸, is known to be robust thermally and hydrothermally and also diffused free due to thicker pore walls and larger pore sizes. The pore wall thickness (31-64 Å) and pore size (260-300 Å) of SBA-15 are much larger than those of MCM-41⁹ (10-15 Å and 20-30 Å, respectively), which has been most commonly used as mesoporous silica. These advantages encouraged us to immobilize salen Mn(III) catalyst on the SBA-15 and design a solid catalyst with similar catalytic properties of homogeneous catalyst, which is known to be a tough challenging task in the field. In this study, a novel mesoporous SBA-15 material containing salen Mn(III) complex has been

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Scheme 1**Scheme 2**

designed, prepared, and applied to the enantioselective epoxidation of unfunctionalized olefins. Comparing with the conventional homogenous catalytic system, the heterogenized catalyst exhibited similar catalytic performance.

The mesoporous silica SBA-15 was synthesized according to the method reported in the literature⁸ and its mesoporous structures were characterized and confirmed by XRD and N_2 adsorption/desorption isotherm. The preparation process of heterogenized catalyst is outlined in **Scheme 1** and **Scheme 2**. In the process, the manganese salen complex was anchored to the solid by the metal through apical ligand coordination. This strategy has a considerable advantage from the economic point of view of and also ensures the purity of the manganese salen complex (sample **2**). The solid was thoroughly washed by diethylether, dried, and characterized by powder XRD, N_2 adsorption/desorption, FT-IR, and elemental analysis. The XRD analysis clearly demonstrated that the mesoporous structure of SBA-15 was preserved during the preparation of the catalyst, and the BET surface areas decreased from $650 \text{ m}^2/\text{g}$ to $293 \text{ m}^2/\text{g}$ after the final coordination reaction. The IR spectroscopy for the series of SBA-15 is shown in **Figure 1**. After modification of SBA-15 mesoporous silica with aminopropyl group and subsequent coordination reactions, the absorption bands at 3433 cm^{-1} and 960 cm^{-1} decreased, indicating the some surface Si-OH group have been replaced. There were two absorption bands in sample **2** (**Figure 1, c**) at 1619 cm^{-1} and 1557 cm^{-1} , these bands were associated to the C=N group in the Salen Mn catalyst. Since the final catalyst

was thoroughly washed with solvent, these FT-IR results demonstrated the formation of the salen Mn complex on the SBA-15 mesoporous structure. Elemental analysis of the SBA-15/NH₂/Mn gave 1.21wt% loading of manganese.

Figure 1 FT-IR spectra of a. SBA-15, b. SBA-15/NH₂, and c. SBA-15/NH₂/Mn

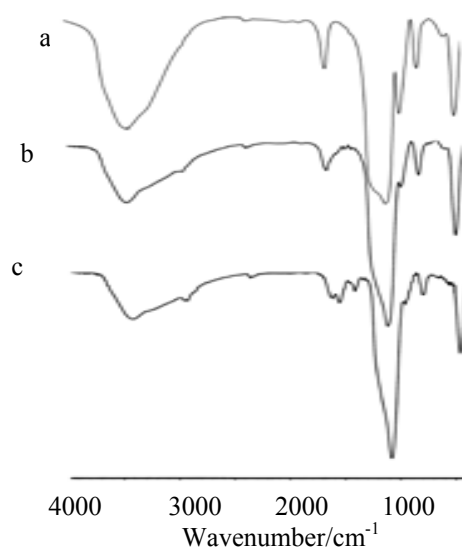


Table 1 Asymmetric epoxidation of *trans*- β -methylstyrene and 1,2-dihydronaphthalene styrene^a catalyzed by homogeneous and heterogenized Mn-salen complex with H₂O₂ as oxidant

Cocatalyst ^c	Reaction time (h)		Conversion ^d (%)		Ee ^e (%)	
	Salen Mn ^{III} Cl	2 ^b	Salen Mn ^{III} Cl	2	Salen Mn ^{III} Cl	2
styrene	1	4	68	54	28	26
NMO	1	4	71	61	29	22
NaHCO ₃	3	4	60	69	14	11
NH ₄ OAc	1	4	72	67	23	34
<i>trans</i> - β -methylstyrene ^f	1	3	54	52	51	53
NMO	2	4	58	62	55	58
NaHCO ₃	1.5	4.5	61	58	54	57
NH ₄ OAc	1.5	4	67	69	63	67
1,2-dihydronaphthalene ^f	1	2.5	68	65	66	64
NMO	1.5	4	70	65	68	67
NaHCO ₃	1.5	4	56	63	54	61
NH ₄ OAc	1.5	4	67	68	64	67

^a reactions were run at 2°C in CH₂Cl₂-CH₃OH(1:1); ^bsalen Mn^{III}Cl : 5% mol, (2): 90 mg of catalyst with the Mn content of 1.21wt%; ^cNMO=N-methylmorpholine N-oxide, the amount of the cocatalyst 40-60 mol%; ^dDetermined by capillary GC, employing *n*-nonane as internal standard; ^eThe ee's for the epoxidation product was determined by GC using CD-chirasil-Dex CB capillary column (25m*0.25mm i.d) and ^f HPLC chiral column OD-H (0.46 cm Φ × 25 cm)

The epoxidation of styrene, *trans*- β -methylstyrene and 1,2-dihydronaphthalene with aqueous H₂O₂ (30%wt) was carried out as the test reaction. The catalytic results are listed in **Table 1**. It can be seen from **Table 1** that the conversion and the enantioselectivity (ee%) of the heterogenized catalyst were almost the same to the corresponding homogeneous catalyst, indicating the effectiveness of the immobilization method developed in this study. The catalytic activities can be improved by introducing cocatalyst NH₄OAc gave slightly better conversion and ee's than the other co-catalysts. We did not find the oxidative destruction of catalyst by H₂O₂ in the reaction with immobilized catalyst, while this side-reaction usually occurred in homogeneous catalytic system. Importantly, we have not observed detectable leach of the complex from the solid to the solution. The catalyst could be recycled effectively several times and the result are listed in **Table 2**. After five times, an 58% ee and 59% yield of epoxide were obtained, using 1,2-dihydronaphthalene as substrate.

Table 2 The recycling experiment for the enantioselective epoxidation of 1,2-dihydronaphthalene using H₂O₂ as oxidant catalyzed by complex **2**^a

Entry	Cycle	Time(h)	Conversion(%) ^d	Ee(%) ^e
1	Fresh	2.5	65	64
2	1	3.5	61	62
3	2	4	61	60
4	3	4	60	59
5	4	4	59	58

a, d, e were the same as in **Table 1**.

In summary, anchoring the salen Mn (III) complex on the mesoporous silica SBA-15 did not change the structure of the SBA-15, while a heterogenized enantioselective catalyst for the epoxidation of alkenes can be constructed. The catalytic performance of the heterogenized catalyst is similar to the homogeneous catalyst, while it offered the advantage of easy separation and recovering.

References and Notes

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