# Chiral salen manganese complex encapsulated within zeolite Y: a heterogeneous enantioselective catalyst for the epoxidation of alkenes

**María J. Sabater, Avelino Corma,* Antonio Domenech, Vicente Fornés and Hermenegildo García**

*Instituto de Tecnología Química C.S.I.C.-U.P.V., Apartado 22012, 46071-Valencia, Spain*

**A chiral (salen)$Mn^{III}$ complex [salen: *trans*-(*R*,*R*)-1,2-bis(salicylideneamino)cyclohexane] analogous to Jacobsen's catalyst is prepared inside the supercages of zeolite Y, showing catalytic activity very similar to that of the chloride complex in the homogeneous phase.**

The use of chiral catalysts has become a powerful methodology in modern synthetic organic chemistry.[1] In this regard, the Sharpless epoxidation of allylic alcohols constituted an authentic breakthrough in this field.[2,3] More recently, Jacobsen and co-workers expanded the scope of the catalytic asymmetric epoxidation to unfunctionalized alkenes with high stereocontrol by using chiral (salen)Mn complexes.[4]

A further logical improvement of this homogeneous catalytic method would consist of the incorporation of the catalyst on to an inorganic support, making it possible to perform the reaction heterogeneously.[5,6] In the present work, we have successfully accomplished for the first time the preparation of a chiral (salen)manganese complex analogous to the Jacobsen catalyst into the supercages of large pore Y zeolite.† The resulting (salen)Mn complex entrapped within Y zeolite exhibits similar catalytic activity as the same complex under homogeneous conditions.

The pore structure of Y zeolite consists of almost spherical 13 Å cavities interconnected tetrahedrally through smaller apertures of 7.4 Å diameter. Molecular modelling predicts that both the salen ligand [salen: *trans*-(*R*,*R*)-1,2-bis(salicylideneamino)-cyclohexane] or the corresponding (salen)$Mn^{III}$ complex can be easily accomodated inside the supercages of Y zeolites. Analogously, it is predicted that the actual Jacobsen's catalyst having four *tert*-butyl groups on the phenyl rings does not fit into the Y zeolite supercages.

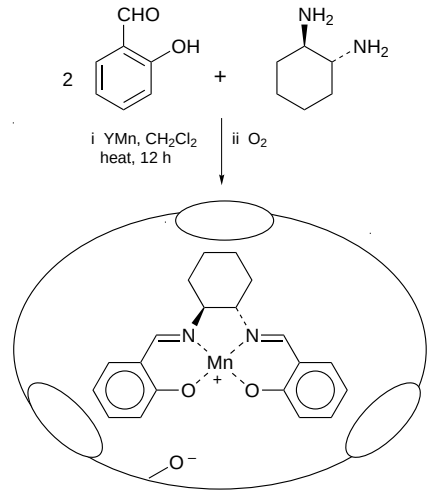
The synthesis of the (salen)$Mn^{III+}$ in the intracrystalline cages of zeolite Y is outlined in Scheme 1. Basically it consists of the condensation of optically active *trans*-(*R*,*R*)-1,2-diamino-cyclohexane and salicylaldehyde around $Mn^{II}$ metal ions resident in the supercages (1 $Mn^{2+}$ every 5 supercages) and a final oxidation step.

Other alternative protocols were found to be less efficient. If both reagents were added simultaneously, an unfavourably large excess of uncomplexed ligand was formed. On the other hand, if chiral diaminocyclohexane was the first reactant added to MnY, the IR spectrum of the corresponding zeolite predominatly showed the bands of unreacted amine.

Samples of (salen)$Mn^{III}$ complex in zeolite Y were fully characterized by thermogravimetry–differential scanning calorimetry (TG–DSC), diffuse reflectance and FTIR spectroscopies and cyclic voltammetry (CV). Thus, the salen/$Mn^{III}$ ratio of the solids quantified by TG–DSC was 1.3 indicating a slight excess of the uncomplexed ligand. The IR spectrum of the zeolite guest after the synthesis shown in Scheme 1 was compared with those recorded for authentic samples of the salen ligand and (salen)$Mn^{III}$Cl (Fig. 1).

As it can be seen from Fig. 1, the spectrum of the (salen)$Mn^{III}$-Y sample coincides with that of the chloride salt of the same complex, thus establishing the purity and identity of the (salen)$Mn^{III}$-Y zeolite. In contrast, the most characteristic band associated with the salen ligand appearing at 1500 $cm^{-1}$ is absent for the zeolite sample, indicating that the amount of uncomplexed ligand is below the detection limit of this technique.

Direct support for the +3 oxidation state of Mn ions as well as their complexation by salen was obtained by electrochemical techniques.[7] The electrochemical behaviour of the (salen)$Mn^{III}$ intrazeolite complex in $Me_2SO$ showed an equilibrium potential of −0.32 V *vs.* SCE. This value matches that recorded for the same complex in a homogeneous phase. Notably, the redox potential of the uncomplexed $Mn^{3+}/Mn^{2+}$ pair would be far more positive. Accordingly, MnY did not show any electrochemical activity .




**Scheme 1**

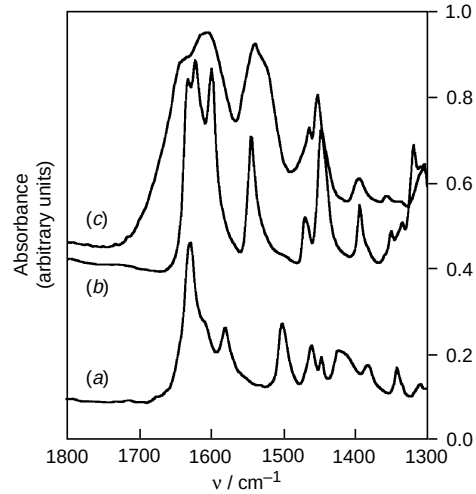



**Fig. 1** Aromatic region of the FTIR spectra of (*a*) the salen ligand, (*b*) (salen)$Mn^{III}$Cl and (*c*) (salen)$Mn^{III}$-Y complexes. Note that the 1535 $cm^{-1}$ absorption characteristic of the complex is present in the spectrum of (salen)$Mn^{III}$-Y sample. In contrast, the salen ligand has a specific 1500 $cm^{-1}$ band as the most distinctive absorption.

EPR measurements confirmed the disappearance of the majority of $Mn^{2+}$ ions from the initial MnY to the final (salen)$Mn^{III}$-Y sample.

In order to determine the performance of the (salen)manganese complexes encapsulated in Y zeolite, the epoxidation of four prochiral alkenes was tested and the results compared with those obtained under homogeneous conditions (Table 1).

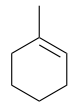
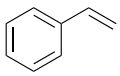
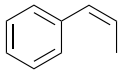
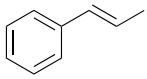
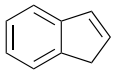
The oxidations were carried out in the presence of catalytic amounts of the (salen)$Mn^{III}Cl$ complex (5 mol%) or 90 mg of the heterogeneous (salen)$Mn^{III}$-Y system by using NaOCl in $CH_2Cl_2$ at 5 °C. Higher reaction temperatures led to a significant decrease in asymmetric induction as well as a dramatic decrease in the epoxide selectivity.

The reactions showed a high chemoselectivity except for compound **1**. Indeed, in most of the cases at 5 °C epoxides were obtained as the main or sole products as detected by GC analysis. Notably, by-products commonly observed for other non-enantioselective zeolite-catalysed epoxidations arising from epoxide scission were absent.[8]

The lower reaction rates obtained with the (salen)$Mn^{III}$-Y heterogeneous catalyst compared to the homogenous counterpart could have been anticipated in view of the restrictions imposed on the diffusion substrate and products through the micropores of the solid, especially when the reaction is run at low temperatures.

With regard to the enantioselectivity, the trisubstituted olefin **1** and styrene **2** gave poor enantiomeric excess. This agrees with previous data on the performance of the Jacobsen's catalyst.[9,10] In contrast, conjugated *trans* olefin **3** and the cyclic indene **4** were epoxidized in moderate to good enantioselectivity both in the homogeneous and the heterogeneous catalysis.

**Table 1** Asymmetric epoxidation of alkenes **1**–**4** catalysed by the (*R*,*R*)-(salen)$Mn^{III}$ complex and NaOCl as oxidant in the homogeneous and heterogeneous phases

| Entry | Olefin[a] | Catalyst[b] | Conversion (%)[c,d] | Epoxide selectivity (%)[c] | Ee (%) |
|---|---|---|---|---|---|
| 1 |  | (salen)$Mn^{III}Cl$ | 37 | 65 | 8 |
| 2 | **1** | (salen)$Mn^{III}$-Y | 11 | 65 | 5 |
| 3 |  | (salen)$Mn^{III}Cl$ | 47 | 80 | 27 |
| 4 | **2** | (salen)$Mn^{III}$-Y | 40 | 61 | 20 |
| 5 |  | (salen)$Mn^{III}Cl$ | 28 | 100 | 74[e] |
| 6 | *cis*-**3** | (salen)$Mn^{III}$-Y | 5 | 76 | 58[e] |
| 7 |  | (salen)$Mn^{III}Cl$ | 23 | 90 | 41 |
| 8 | *trans*-**3** | (salen)$Mn^{III}$-Y | 11 | 100 | 24 |
| 9 |  | (salen)$Mn^{III}Cl$ | 30 | 100 | 60 |
| 10 | **4** | (salen)$Mn^{III}$-Y | 20 | 96 | 50 |

[a] Reactions were run at 5 °C in $CH_2Cl_2$. [b] (salen)$Mn^{III}Cl$, 5% mol; (salen)Mn-Y, 90 mg of catalyst with a complex content of 3.8%. [c] Determined by quantitative capillary GC analysis. [d] Reaction time: 2–3 h using (salen)$Mn^{III}Cl$ and 12–15 h for (salen)$Mn^{III}$-Y catalyst. [e] Ee of *trans* epoxide.

Although the ees obtained using (salen)$Mn^{III}$-Y and (salen)-$Mn^{III}Cl$ follow the same pattern, we consistently noticed somewhat lower values for the zeolite-bound catalyst. This can be interpreted as a combination of two unfavourable factors: (i) the occurrence of a non-catalysed, unselective epoxidation route in the liquid phase and/or (ii) the existence of residual amounts of uncomplexed $Mn^{2+}$ acting as catalytic sites.

The above point raises the question of how to assess that the reaction is taking place inside the zeolite micropores. The simplest straightforward way to address this point is to determine the inactivity of the heterogeneous (salen)$Mn^{III}$-Y catalyst by using reagents of larger dimensions than the pore windows of zeolite host. Under these conditions the homogeneous (salen)$Mn^{III}Cl$ counterpart must be still an efficient epoxidation catalyst.

Thus, we found that a iodosylbenzene derivative obtained by basic hydrolysis of [bis(trifluoroacetoxy)iodo]benzene[11] gives very similar results to those presented in Table 1 using NaOCl in the presence of (salen)$Mn^{III}Cl$. However, FABMS established that the structure of this iodosylbenzene sample was not monomeric but likely to be a cyclic oligomeric precursor of PhIO. Therefore, this bulky reagent would be size excluded from the 7.4 Å faujasite pore windows. Accordingly, no conversion could be observed in the epoxidation of alkenes **2**–**4** in the presence of (salen)$Mn^{III}$-Y catalyst. In addition, this lack of activity of the (salen)$Mn^{III}$-Y catalyst compared to the 43% conversion achieved using (salen)$Mn^{III}Cl$ indicates that no leaching of Mn ions from the interior of the zeolite to the solution occurs and also that the external surface sites play a very minute role in the overall catalytic process. To further establish the lack of Mn leaching, we performed chemical analysis of the liquid phase after the reaction. No Mn ions could be detected.

All the enantioselective enzymatic systems in nature have in common the incorporation of the active sites into a confined space defined by the tertiary protein structure. Our chiral (salen)$Mn^{III}$-Y catalyst mimics this strategy: the rigid, inorganic framework of the zeolite determines the reaction cavity surrounding the active complex.

## Footnotes

* E-mail: itq@upv.es

† Although no article has been published yet, a referee has indicated that a similar chiral (salen)Mn complex inside zeolite EMT has been claimed by T. Bein, ACS Chiral Catalysis Symposium, Orlando, 1996.

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