Stereoselective epoxidation of R-(+)-limonene over Mn(III) salen complexes immobilized in Al-MCM-41

Jairo A. Cubillos*, María T. Vargas, Juliana Reyes, Aída L. Villa and Consuelo Montes de Correa
Grupo catálisis Ambiental, Universidad de Antioquia, Sede de Investigación universitaria (SIU), carrera 53 No 61-30, Medellín (Colombia)
*jclobo@udea.edu.co

Introduction

Limonene epoxide is a key raw material for fine chemicals. Limonene has two olefinic bonds (1,2 and 8,9), therefore two types of diastereomers (*cis* and *trans*) are expected for each of the epoxide products [1]. Chiral Mn(III) Schiff base complexes with a N_2O_2 coordination sphere, generally known as Mn(III) salen complexes, have been reported as highly enantioselective catalysts for the epoxidation of unfunctionalized alkenes in homogeneous phase. In particular, the Jacobsen's catalyst is widely used at laboratory scale [2]. Also, it is possible to perform diastereoselective epoxidation of chiral molecules using a cheap achiral catalyst [3]. Hoelderich and Bhattacharjee independently reported the diastereoselective epoxidation of R-(+)-limonene using recycable chiral heterogeneous catalysts [2]. Ratnasamy and coworkers proved that the use of an achiral heterogeneous catalyst promotes these type of reactions [1]. However, the tert-butyl groups on salen ligand responsible of high activity were not involved. Here, we report the stereoselective epoxidation of R-(+)-limonene with Jacobsen's catalyst in their achiral and chiral forms immobilized in Al-MCMC-41. *In situ* generated dimethyldioxirane (DMD) was the oxidizing agent since milder reaction conditions can be accomplished with this oxidant [4].

Materials and Methods

The appropriate amine, 3,5 di-tert-butylsalycilaldehyde and $Mn(CH_3CO_2)_2$ were used in the synthesis of the Mn(III) salen complexes. These complexes were immobilized in Al-MCM-41 by treating Mn-Al-MCM-41 with the corresponding salen ligand. The purity of Mn(III) salen complexes was checked by FT-IR and TGA while Mn chemical analysis, FT-IR, TGA and N_2-Sorption were used to prove the immobilization process. Reaction mixture consisted of mixture of R-(+)-limonene, $NaHCO_3$, catalyst and acetone to which an Oxone®/H_2O solution was added dropwise, controlling pH in the range 8-8.5. With this procedure it is expected *in situ* DMD generation from Oxone® ($KHSO_5$ as active component) and acetone.

Results and Discussion

Figure 1 illustrates the immobilization processes followed here. Table 1 shows results of catalytic activity. Without any catalyst, epoxidation is accomplished with poor diastereoselectivity (23 %). In the presence of homogeneous catalysts the diastereomeric excess (de) to *cis*-(+)-1,2-limonene epoxide is remarkably increased in the presence of both chiral and achiral homogeneous catalysts. Although diastereomeric excesses remarkably decreased, the highest productivities were obtained over heterogenized catalysts. Leaching may be avoided by catalyst pretreatment with Oxone® even though a decreased TON was observed.

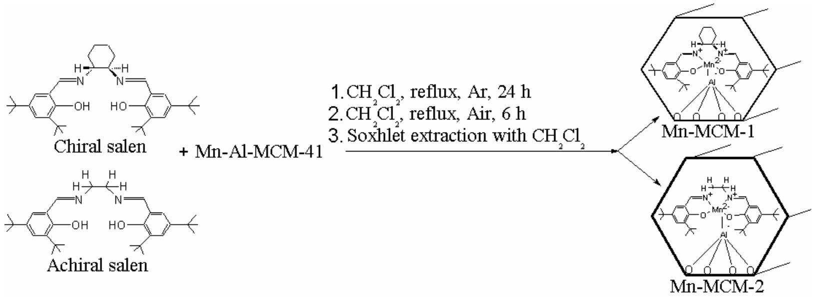

Figure 1. Al-MCM-41 immobilization of chiral and achiral Mn(III) salen complexes.

Table 1. Catalytic activity [a], selectivity and diastereomeric excess (de) to *cis*-(+)-1,2-limonene epoxide.

Catalyst	Conversion (%)	Selectivity to 1,2 R-(+)- limonene epoxide (%)	de (%)	TON (mg *cis*-(+)-1,2-limonene epoxide / mg catalyst)
None	53	34	23	-
Chiral	85	100	56	17
Achiral	80	100	50	16
Mn-MCM-1[b]	100	68	34	69
Mn-MCM-2[b]	81	81	36	68
Mn-MCM-1[c]	60	49	25	28
Mn-MCM-1[c,d]	60	58	22	32
Mn-MCM-2[c]	70	62	24	41
Mn-MCM-2[c,d]	71	64	22	42

[a] R-(+)-limonene/Oxone®/catalyst = 5/2/30 (100) mmol/mmol/mg homogeneous catalyst (mg heterogeneous catalyst); $NaHCO_3$ = 1mmol; acetone = 30mL; H_2O = 20mL; room temperature. [b] Reaction mixture coloration was observed. [c] Catalyst was treated with Oxone® before reaction. [d] Reused three times.

Significance

Achiral and chiral Mn(III) salen complexes give similar diasteromeric excess for the stereoselective epoxidation of R-(+)-limonene. Under the conditions of this study, these results suggest that the formation of the chiral center in the epoxide product is mainly dominated by the substrate chiral center rather than by the catalyst chiral center.

References

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