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Preparation, Catalytic Properties and Recycling Capabilities Jacobsen's Catalyst

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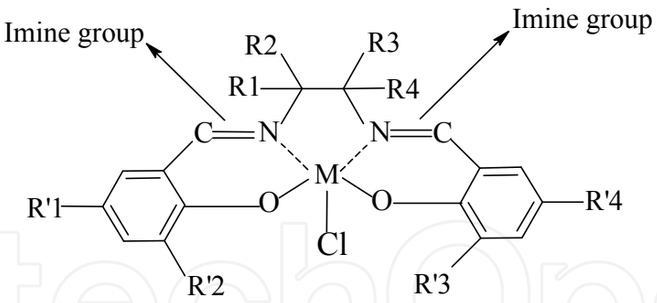
1. Introduction

Metal salen complexes, such as the Jacobsen's catalyst, have attracted much interest in the last few decades because of their unique catalytic activity, especially as olefin epoxidation catalysts, in the presence of terminal oxidants like iodosylbenzene (PhIO), sodium hypochlorite (NaOCl), and *meta*-chloroperoxybenzoic acid (*m*-CPBA) (Gladasi, 2007). Salen ligands of Jacobsen's catalyst bind manganese ions through four atoms, two nitrogen and two oxygen atoms. This tetradentate-binding motif is reminiscent of the porphyrin framework in the heme-based oxidative enzymes (Canali & Sherrington, 1999). Nonetheless, salen derivatives are more easily synthesized than porphyrins and their structures are more easily manipulated to create an asymmetric environment around the active metal site (Canali & Sherrington, 1999). However, this homogeneous catalyst cannot be separated from the reaction media and, subsequently, cannot be recycled. Moreover, it suffers deactivation in homogeneous phase by either formation of dimeric μ-oxo-manganese (IV) species, which are inactive in the olefin epoxidation or oxidative degradation of the salen ligand through the imine group (Figure 1) (Xia et al., 2005). The conventional ways to solve these problems are to immobilize Jacobsen-type catalysts onto solid supports. The last decade has witnessed an intense research effort to heterogenise Jacobsen-type catalysts, and in general chiral manganese(III) salen complexes, using several types of supports in order to make them recyclable as well as economical (Murzin et al., 2005). Reports on the heterogenization of Jacobsen-type catalysts have been centered on their covalent binding to organic polymers (Clapham et al., 2001) and on their encapsulation, entrapment, adsorption and covalent attachment to porous inorganic supports, such as zeolites, Si-MCM-41, Al-MCM-41 and clays (Cubillos, 2010; Dasa, 2006; Kureshy, 2006), and also on activated carbon (Mahata et al., 2007). Unfortunately, the catalytic activity of the recovered catalyst decreases during the catalytic tests of reuse. It is found that isolating Mn(III) salen complexes onto a solid support increases the catalyst stability (Baleizaõ & García, 2006) by suppressing the formation of inactive dimeric μ-oxo manganese(IV) species. However, the deactivation route by ligand oxidation cannot be avoided by anchoring the catalyst to a solid matrix, since it depends on the oxidation conditions. On the other hand, the immobilized catalysts usually lead to partial loss of activity and/or enantioselectivity as compared to their analogous homogeneous catalysts (Baleizaõ & García, 2006). It is well known that in homogeneous phase, the catalyst acquires an appropriate geometric configuration that promotes both, the



M = Mn, Cr, Co, Cu, V, Ru, Fe, Al, Ti

R1, R2, R3, R4 = H, alkyl or phenyl group

R'1, R'2, R'3, R'4 = H, nitro, alkyl, aryl or alcoxy group

Fig. 1. Chemical structure of metal salen complexes.

oxygen transfer from oxo-Mn(V) active species to the double bond of olefin and chiral induction (Adam et al., 2000). In contrast, when the catalyst is not free to move due to the influence of the solid support, an inappropriate geometrical configuration can be obtained (Fan et al., 2002). In addition to that, structural modification of either the catalyst or the solid support during the immobilization process, generally lead to diminished catalytic activity (Mastrorilli & Nobile, 2004). The most common immobilization methods by covalent bond modify one or two tert-butyl groups of the salen ligand. It is known that the tert-butyl groups are very important, since they define the optimal trajectory of the incoming olefin towards the oxo-Mn(III) active species (Linde et al., 2005). In summary, compared with the homogeneous counterparts, some of the immobilized complexes often suffer from various disadvantages, such as poor activity, leaching of the active species into the reaction medium, and low substrate accessibility (Baleizaõ & García, 2006). Therefore, for industrial practical merit and academic interest of homogeneously catalyzed reactions, the development of an efficient strategy for catalyst recovery is still challenging.

An alternative convenient and economical strategy is to adjust the solubility of homogeneous catalysts by varying the reaction conditions, resulting in the direct separation of the catalysts during the reaction (Kureshy et al., 2001). Recently, I and my colleagues described that using dimethyldioxirane (DMD) as oxidizing agent for the epoxidation of R-(+)-limonene and *cis*-ethyl cinnamate with Jacobsen-type catalysts could facilitate product isolation and catalyst recovery by segregating the catalysts into a solid phase during the reaction (Cubillos et al., 2009). Limonene di-epoxide was the main product from limonene, whereas an epoxide was obtained with 78% e.e in the case of *cis*-ethyl cinnamate. Moreover, it was reported that catalyst stability towards the oxidative degradation could be enhanced in the reaction medium, using DMD as oxidizing agent (Cubillos et al., 2009). On the other hand, it was found that the stereogenic center of the pure enantiomerically Jacobsen's catalyst did not influence the catalytic activity for the epoxidation of R-(+)-limonene (Cubillos et al., 2010).

Here I report the preparation and the catalytic properties as well as recycling capabilities of pure enantiomerically Jacobsen's catalysts (R,R-Jacobsen and S,S-Jacobsen) and its racemic form for epoxidation of R-(+)-limonene and *cis*-ethyl cinnamate with *in situ* generated DMD as oxidant. In order to compare the activity, recovery and reuse of the catalysts with DMD,

other oxidizing agents (NaOCl and *m*-CPBA) most commonly used, were employed for R-(+)-limonene epoxidation with R,R-Jacobsen as catalyst. The influence of catalyst optical configuration on catalytic performance for this reaction is also revised.

2. Experimental section

The main reagents used for the synthesis of Jacobsen-type catalysts were 2,4-di-tert-butylphenol, tin(IV) chloride (99%, Aldrich®), paraformaldehyde (99.5%, Aldrich®), L-(+)-tartaric acid (99.5%, Aldrich®), D-(–)-tartaric acid (99, Aldrich®), *cis/trans* 1,2-diaminocyclohexane (99%, Aldrich®), potassium carbonate (99.995%, Aldrich®), manganese acetate tetrahydrate (99%, Aldrich®) and lithium chloride (99.99%, Aldrich®). All these materials were directly used as received. The solvents were absolute ethanol, chloroform, acetone and dichloromethane. 3,5-di-tert-butyl salicylaldehyde was prepared from the formylation of 2,4-di-tert-butylphenol using paraformaldehyde as reactant and tin(IV) chloride as catalyst (Deng & Jacobsen, 1992). (R,R)-1,2-diammoniumcyclohexane and (S,S)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt were prepared from the racemic resolution of *cis/trans* 1,2-diaminocyclohexane with L-(+)-tartaric acid and D-(–)-tartaric acid, respectively (Deng & Jacobsen, 1992). Other reagents included R-(+)-limonene (97%, Aldrich®), ethyl phenylpropiolate (98%, Aldrich®), Lindlar's catalyst (5 wt.% on calcium carbonate, Aldrich®), Oxone® ($2KHSO_5 \bullet KHSO_4$, K_2SO_4, Aldrich®), manganese(II) acetate tetrahydrate (99%, Aldrich®), and sodium bicarbonate (Merck), aqueous sodium hypochlorite (NaOCl, 7% active chlorine basis, Carlo Erba), 4-phenylpyridine N-oxide (98%, Aldrich®), *meta*-chloroperoxybenzoic acid (*m*-CPBA, 77%, Aldrich), 4-methylmorpholine N-oxide (97%, Aldrich®). *Cis*-ethyl cinnamate was prepared from the partial hydrogenation of ethyl phenylpropiolate using the Lindlar's catalyst (Larrow & Jacobsen, 1994).

Different salen ligands R,R-Jacobsen, S,S-Jacobsen and racemic were prepared according to the methods previously described (Deng & Jacobsen, 1992), by condensing the appropriate diamine (3.5 mmol) and 3,5-di-tert-butyl salicylaldehyde (7.0 mmol), for 2 h, using ethanol as a solvent. Upon reaction, completion of a yellow–orange precipitate appeared. These precipitates were filtered and dried under vacuum. The obtained solids were characterized by FT-IR (Bahramian et al., 2006). The Jacobsen's catalysts R,R-Jacobsen, S,S-Jacobsen and Jacobsen racemic (Figure 2), were prepared as previously described (Deng & Jacobsen, 1992). Ethanolic solutions of 3.0 mmol of different ligands, and 3.3 mmol of manganese (II) acetate tetrahydrate were refluxed, for 1 h. During reflux, a change in the color of the solution from yellow–orange to dark-brown was observed. The manganese complexes were recrystallized in heptane and dried under vacuum. The FT-IR and DR UV–Vis spectral bands of all complexes were found to be identical to those reported (Bahramian, 2006; Chaube, 2005).

R,R-Jacobsen, S,S-Jacobsen and Jacobsen racemic catalysts were then used as catalysts for the epoxidation of R-(+)-limonene (1) and *cis*-ethyl cinnamate (2). In a standard procedure, 1.0 mmol of substrate, 1.2 mmol of sodium bicarbonate and 0.05 mmol of catalyst were dissolved in 4 mL of acetone. A buffer solution (aqueous $NaHCO_3$, 5 % wt) was added to bring the pH in the range between 8.0-8.5 (mixture A). In another vessel, 2.0 mmol of $KHSO_5$ (Oxone®) was dissolved in 4 mL of water (mixture B). While mixture A was being stirred, mixture B was slowly added, keeping the pH in the range 8.0 - 8.5 using $NaHCO_3$ solution (5 % w/w aqueous). When mixture B was completely added, stirring was stopped and the

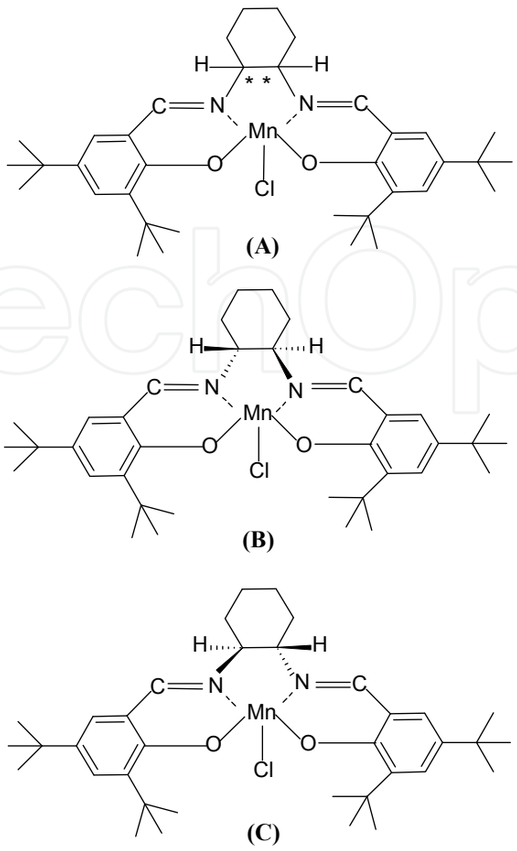


Fig. 2. Chemical structure of Jacobsen type catalysts. A: Racemic Jacobsen, B: R,R-Jacobsen, C: S,S-Jacobsen.

formed solids separated by filtration and/or centrifugation. The liquid phase was extracted with dicloromethane in a separation funnel and analyzed by GC. The solid phase was washed with sufficient water up to reach a constant weight in the obtained residue. This dark brown residue (catalyst) was easily dissolved in acetone and thus ready for recycling. Also, the chemical identity of this residue was analyzed by FTIR.

An Agilent Technologies 7890A gas chromatograph (GC), equipped with a DB-1 capillary column (50 m long, 0.32 mm ID and 1.20 mm film thickness) and a FID detector was used for the analysis of solvent purity, olefin and oxidation products. Ultra high pure helium was used as carrier gas (30 mL/min). The injection port temperature was kept at 300 ˚C. For separation of R-(+)-limonene the column temperature was programmed between 80 and 140 ˚C while for *cis*-ethyl cinnamate it was kept isothermal at 140 ˚C. The area normalization method was used to determine conversion, selectivity and relative yield. The enantiomeric excess (ee) for the single epoxide derived from *cis*-ethyl cinnamate epoxidation was determined by GC using a chiral capillary column, i.e. Betadex GTA (60 m long, 250 mm ID and 0.25 mm film thickness). In this case, a commercially available 3-ethyl-phenylglycidate (*cis*/*trans* = 10/90, Aldrich) racemic mixture was used. In the case of the chiral epoxides derived from R-(+)-limonene, 1,2-limonene oxide (97%, mixture of *cis* and *trans*, Aldrich) was used. Limonene diepoxide was prepared by oxidation of R-(+)-limonene (1.0 mmol) oxide using *m*-CPBA (5.0 mmol) as oxidizing agent and confirmed by GC–MS. The optical configuration was assigned by

comparing the chromatogram of our products with those of *cis*-ethyl cinnamate isomers available in literature (Steiner et al., 2002). Also, isolated yields of the major epoxide product for either substrate were calculated. Thus, the major epoxide originating from the *cis*-ethyl cinnamate oxidation was purified by short-path distillation (110 °C and 0.5 mmHg), while in the case of R-(+)-limonene, diepoxide was collected at 140 °C and 0.5 mmHg.

In order to compare the catalytic activity, recovery and reuse of catalysts with DMD, other oxidizing agents such as NaOCl and *m*-CPBA were explored for R-(+)-limonene epoxidation according to reported conventional methods (Wang et al., 2006), using the same molar ratio of substrate/oxidant (0.5 mmol/mmol), substrate/catalyst (20 mmol/mmol), reaction time (30 min) and reaction temperature (25 °C) as DMD.

3. Results and discussion

Figure 3 shows the FTIR spectra of the salen ligands and their corresponding catalysts. The salen ligands show a characteristic band around 1620 cm^{-1}, which is associated with the vibrations of the imine group (HC=N) (Bahramian et al., 2006). In the catalyst samples, this band is displaced towards lower wavelengths (1600-1590 cm^{-1}) as the first evidence of the formation of the organometallic complex. Additionally, characteristic bands at 1530 (C-O), 550 (Mn-O) and 480 cm^{-1} (Mn-N) are also associated with the complexation of manganese by the salen ligand (Bahramian et al., 2006).

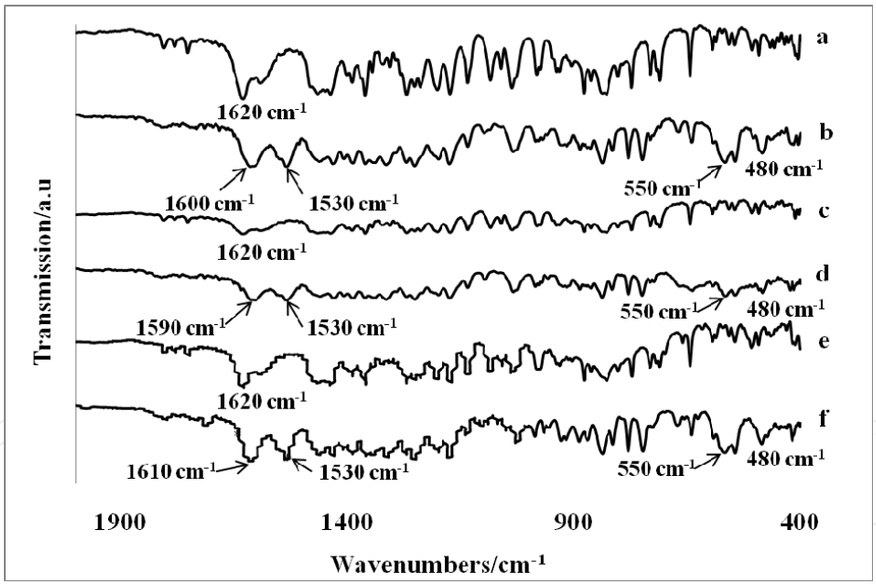


Fig. 3. FT-IR Spectra of (R,R) Jacobsen's ligand (a), (R,R) Jacobsen's catalyst (b), (S,S) Jacobsen's ligand (c), (S,S) Jacobsen's catalyst (d), Jacobsen's racemic ligand (e), Jacobsen's racemic catalyst (f).

Figure 4 shows DR UV-vis spectra of the salen ligands and their corresponding catalysts. The salen ligands exhibit absorption bands at 265 nm and 335 nm. These bands are attributed to π→π* transitions. The band at 265 nm has been assigned to the benzene ring and the one at 335 nm, to the imino groups (Chaube et al., 2005). The imino π→π* transitions in the Mn salen complexes is shifted to larger wavelengths due to metal coordination,

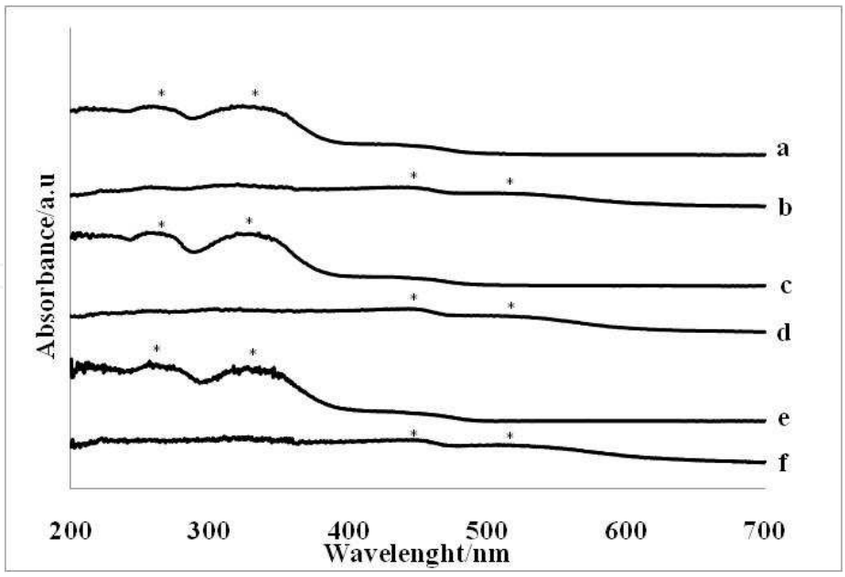


Fig. 4. DR UV-vis Spectra of (R,R) Jacobsen's ligand (a), (R,R) Jacobsen's catalyst (b), (S,S) Jacobsen's ligand (c), (S,S) Jacobsen's catalyst (d), Jacobsen's racemic ligand (e), Jacobsen's racemic catalyst (f).

confirming the formation of Mn(III) salen complex (Chaube et al., 2005). UV–Vis and FT-IR spectra revealed that the salen ligands are unaffected and are not decomposed upon coordination of the organo-funtional groups with manganese (Chaube et al., 2005).

R,R-Jacobsen, S,S-Jacobsen and Jacobsen racemic catalysts were examined in the liquid phase oxidation reaction of *cis*-ethyl cinnamate and R-(+)-limonene using *in situ* generated DMD as oxidizing agent. Different oxidation products were obtained, depending on the substrate type. Figures 5 and 6 outline the test reactions. Di-epoxides appear as the main products from R-(+)-limonene oxidation (Figure 5), while a single epoxide ((2R,3R)-*cis* ethyl-3-phenylglycidate) was produced from *cis*-ethyl cinnamate oxidation (Figure 6). Similarly to the previously reported experiments of olefins oxidation (Cubillos, 2009, 2010), the Jacobsen type catalyst was easily separated from the obtained solid phase at the end of reaction.

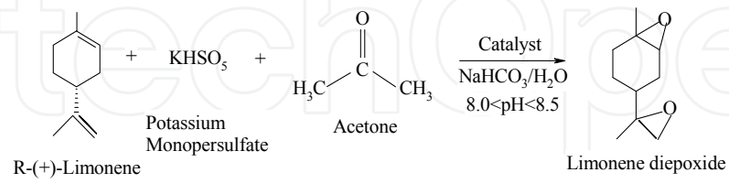


Fig. 5. Selective oxidation of R-(+)-limonene (1).

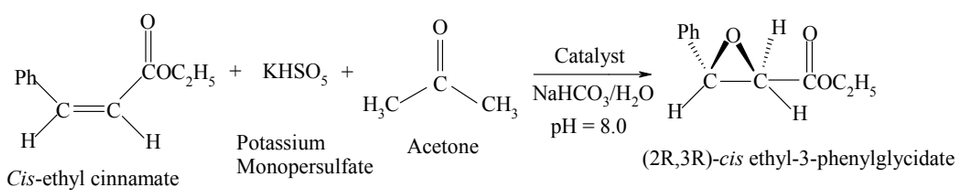


Fig. 6. Enantioselective oxidation of *cis*-ethyl cinnamate (2).

The results of catalytic activity and recyclability are collected in Tables 1 and 2. In the absence of catalyst, reaction was observed for R-(+)-limonene (conversion 53 % and relative rates of reaction 0.145 mol/Lt×h). In this case, 79% selectivity to limonene diepoxide with 46% relative yield and 30% isolated yield was achieved. 1,2-limonene oxide was obtained as secondary product with very low selectivities (Table 1, entry 1,). In contrast, no reaction was observed using *cis*-ethyl cinnamate as substrate (Tables 1 and 2, entry 8). It is known that unfunctionalized olefins are more reactive than its functionalized counterparts when Jacobsen type catalysts are used (Porter & Skidmore, 2000).

Entry	Substrate	Catalyst	Conversion (%)	Epoxide selectivity (%)	Diepoxide selectivity (%)	Relative yield[h] (%)
1	(**1**)[a]	None	58	18[e]	79[g]	46[i]
2	(**1**)[a]	I	100	5[e]	93[g]	93[i]
3	(**1**)[a]	II	100	3[e]	93[g]	93[i]
4	(**1**)[a]	III	100	4[e]	95[g]	95[i]
5	(**1**)[b]	I	99	7[e]	90[g]	89[i]
6	(**1**)[c]	I	98	5[e]	87[g]	85[i]
7	(**1**)[d]	I	98	8[e]	90[g]	88[i]
8	(**2**)[a]	None	0	-	-	0
9	(**2**)[a]	II	18	88[f]	-	16[j]
10	(**2**)[a]	III	20	84[f]	-	17[j]
11	(**2**)[a]	I	15	90[f]	-	14[j]
12	(**2**)[b]	II	12	82[f]	-	10[j]
13	(**2**)[c]	II	8	83[f]	-	7[j]
14	(**2**)[d]	II	6	82[f]	-	5[j]

[a] Reaction conditions: substrate = 1.0 mmol; $KHSO_5$ = 2.0 mmol (from Oxone®), catalyst = 0.05 mmol; acetone = 4.0 mL; water = 4.0 mL; reaction time = 30 min. [b] First reuse. [c] Second reuse. [d] Third reuse. [e] Selectivity to 1,2-limonene oxide. [f] Selectivity to ethyl-3- phenylglycidate (sum of *cis* and *trans*). [g] Sum of the four diepoxides of R-(+)-limonene. [h] Relative yield = Conversion×Selectivity/10,000. [i] Relative yield to the diepoxides. [j] Relative yield to ethyl-3-phenylglycidate (sum of *cis* and *trans*).

Table 1. Results of catalytic activity and reutilization

Similar yields (relative yields 93-95% and isolated yields 56-60%) to limonene diepoxide were reached with all catalysts, while in the absence of catalyst 46% and 30% respectively, were obtained. This finding suggests that the chiral center of enantiomerically pure (R,R and S,S-Jacobsen) appear to have little or no influence on the catalytic activity; rather the state of coordination given by the salen ligand to the manganese appears to be crucial. Here, the contribution of the catalyst is proven once again by an increase of both R-(+)-limonene conversion (or relative rates of reaction) and selectivity to limonene diepoxide (sum of the four diepoxides of R-(+)-limonene). None of the four diepoxides of R-(+)-limonene predominated. In contrast, the catalytic oxidation of *cis*-ethyl cinnamate offers the possibility

Entry	Substrate	Catalyst	Relative rate of reaction[e] (mol/lt×h)	Enantiomeric excess (%)	Isolated yield (%)
1	(**1**)[a]	None	0.145	-	30[h]
2	(**1**)[a]	I	0.25	-	56[h]
3	(**1**)[a]	II	0.25	-	57[h]
4	(**1**)[a]	III	0.25	-	60[h]
5	(**1**)[b]	I	0.25	-	52[h]
6	(**1**)[c]	I	0.245	-	53[h]
7	(**1**)[d]	I	0.245	-	50[h]
8	(**2**)[a]	None	0	-	0
9	(**2**)[a]	II	0.045	78[f]	11[i]
10	(**2**)[a]	III	0.050	55[g]	9[i]
11	(**2**)[a]	I	0.038	0	7[i]
12	(**2**)[b]	II	0.030	76[f]	7[i]
13	(**2**)[c]	II	0.020	74[f]	5[i]
14	(**2**)[d]	II	0.015	73[f]	4[i]

[a] Reaction conditions: substrate = 1.0 mmol; $KHSO_5$ = 2.0 mmol (from Oxone®);catalyst = 0.05 mmol; acetone = 4.0 mL; water = 4.0 mL. Reaction time = 30 min. [b] First reuse. [c] Second reuse. [d] Third reuse. [e] Relative rate of reaction = Conversion×initial mol/reaction volume×reaction time. [f] Enantiomeric excess of (2R,3R)-cis-ethyl-3-phenylglycidate over (2S,3S)-cis-ethyl-3-phenylglycidate. [g] Enantiomeric excess of (2S,3S)-*cis*-ethyl-3-phenylglycidate over (2R,3R)-*cis*-ethyl-3-phenylglycidate. [h] Isolated yield to R-(+)-limonene diepoxides. [i] Isolated yield to ethyl-3-phenylglycidate (sum of *cis* and *trans*).

Table 2. Results of catalytic activity and reaction rates

to epoxidize the unique C=C double bond located in its chemical structure. In order to perform enantioselective epoxidation, a pure enantiomerically catalyst is required, which can be reached either using R,R-Jacobsen or S,S-Jacobsen. In general, good selectivities to ethyl-3-phenylglycidate (sum of *cis* and *trans*, 84-90%) and good enantiomeric excesses to (2R,3R)-*cis*-ethyl-3-phenylglycidate (78%) were obtained with R,R-Jacobsen. In contrast, lower yields were reached (relative yields 16 and isolated yields 11). Additionally, it is worth to note that the product stereochemistry is strongly dependent on the absolute configuration of catalyst. Thus, *cis*-ethylcinnmate with R,R-Jacobsen gives(2R,3R)-*cis*-ethyl-3-phenylglycidate (Table 2, entry 9), whereas R-(+)-limonene with S,S-Jacobsen gives (2S,2S)-*cis*-ethyl-3-phenylglycidate (Table 2, entry 10). This shows clearly the specificity of a pure enantiomeric catalyst for inducing the preferential formation of the observed product.

Table 3 shows the results of catalytic activity and catalyst recovery for R-(+)-limonene epoxidation using the R,R-Jacobsen catalyst and three oxidants: DMD, NaOCl and *m*-CPBA. For these experiments, Figure 7 shows the spectra of the fresh and used catalyst after reaction with either oxidant. As listed in Table 3, the largest conversion was obtained with DMD (100%), although different selectivities were obtained. Thus, 1,2-limonene oxide was the major product when NaOCl and *m*-CPBA were used as oxidizing agents, obtaining

Entry	Oxidizing agent	Conversion (%)	selectivity (%)	Process of catalyst recovery
1	None	0	-	-
2	NaOCl[a]	65	75[d]	Vacuum distillation
3	*m*-CPBA[b]	35	95[d]	Vacuum distillation
4	DMD[c]	100	93[e]	Centrifugation and filtration

[a] R-(+)-limonene = 1.0 mmol; NaOCl = 2.0 mmol (0.05 M aqueous Na2HPO4 solution) ; 4-phenyl pyridine N-oxide = 0.4 mmol; R,R-Jacobsen = 0.05 mmol; dichloromethane = 4 mL Reaction time = 30 min. [b] R-(+)-limonene = 1.0 mmol; *m*-CPBA= 2.0 mmol; 4-methylmorpholine N-oxide = 5 mmol; R,R-Jacobsen = 0.05 mmol; dichloromethane = 4 mL; Reaction time = 30 min. [c] R-(+)-limonene = 1.0 mmol; KHSO5 = 2.0 mmol (from Oxone®); catalyst = 0.05 mmol; acetone = 4.0 mL; water = 4.0 mL; Reaction time = 30 min. [d] Selectivity to 1,2-limonene oxide; [e] Selectivity to R-(+)-limonene diepoxides (sum of the four diepoxides of R-(+)-limonene).

Table 3. R-(+)- limonene epoxidation using R,R-Jacobsen as catalyst . Effect of the oxidizing agent.

about 95% with *m*-CPBA. In the case of DMD, R-(+)-limonene diepoxides, were the major products. These differences in selectivities can be associated to the easy segregation of the catalyst. Presumably, this phenomenon creates active sites in the precipitated solid that promotes double epoxidation. It has been reported that the catalyst is not separable by means of physical-mechanical methods, when NaOCl and *m*-CPBA were used as oxidizing agents (Abdi et al., 2004). In these cases, a distillation process under vacuum (160 °C and 0.08 MPa) was required in order to separate the catalyst from reaction products, whereas with DMD the catalyst was isolated by physical-mechanical separation methods. On the other hand, figure 7 reveals that the catalyst exhibited the best stability to the oxidative degradation when *in situ* generated DMD was used as the oxidizing agent, since the main band associated to the Mn(III) salen complexes (1530 cm^{-1}) is still present in the FTIR spectrum, where DMD was used as oxidizing agent. Other important bands associated to the Mn-O (550 cm^{-1}) and Mn-N (480 cm^{-1}) stretching vibrations are slightly displaced towards a lower wavelength.

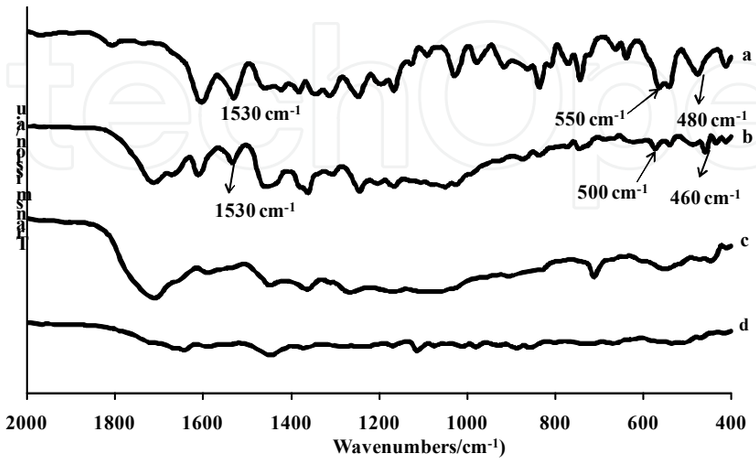


Fig. 7. FT-IR Spectra of the (R,R) Jacobsen's catalyst used with different oxidizing agents: fresh catalyst (a), DMD (b), NaOCl (c) and m-CPBA (d).

Finally, catalyst reuse was explored for both reactions. As can be observed in Tables 1 and 2, catalysts experienced a slight decrease in their initial catalytic activity through three consecutive runs in both reactions. The catalyst was segregated into a solid phase, while the reaction products remained in the liquid phase. This allowed the easy separation of catalyst and reaction products. On the other hand, Figure 8 shows the spectra of the catalyst used in three cycles. Clearly, it is observed that the main bands associated to the Mn(III) salen complexes are retained in the used catalysts. It indicates that the catalyst is very stable to the reaction conditions during three consecutive runs, whereas with oxidizing agents like NaOCl and *m*-CPBA the catalyst was deactivated in the first run (Figure 7). Therefore, the slight loss of catalytic activity with DMD is associated to physical loss of the catalyst during the isolation process rather than to oxidative degradation.

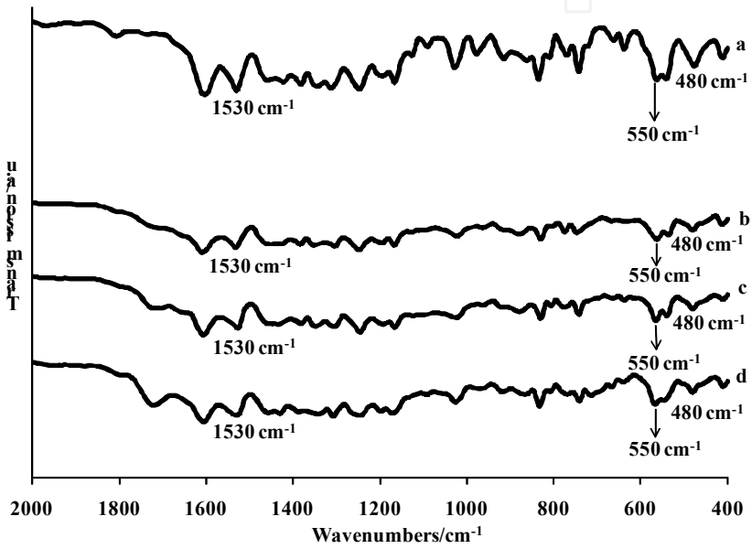


Fig. 8. FT-IR Spectra of the (R,R) Jacobsen's catalyst used in various run: fresh catalyst (a), second run (b) third run (c) fourth run.

4. Conclusion

Diepoxides were the main products from the oxidation of R-(+)-limonene, whereas a monoepoxide is obtained in the case of the catalytic oxidation of *cis*-ethyl cinnamate. In the latter case, a pure enantiomerically catalyst is required, while the Jacobsen racemic catalyst was sufficient in the case of the catalytic oxidation of R-(+)-limonene. Given that the catalytic activity of the three catalysts is very similar for R-(+)-limonene epoxidation and considering that the unique difference among the three catalysts is its stereogenic center located in the bond C1-C2 of the 1,2-diamino cyclohexane component, I conclude that the catalytic activity is not dependent on the stereogenic center. The catalyst could be recycled three times without appreciable loss of its initial activity.

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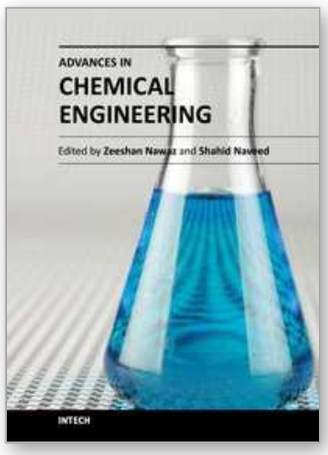

Advances in Chemical Engineering

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Chemical engineering applications have been a source of challenging optimization problems in terms of economics and technology. The goal of this book is to enable the reader to get instant information on fundamentals and advancements in chemical engineering. This book addresses ongoing evolutions of chemical engineering and provides overview to the sate of the art advancements. Molecular perspective is increasingly important in the refinement of kinetic and thermodynamic molding. As a result, much of the material was revised on industrial problems and their sophisticated solutions from known scientists around the world. These issues were divided in to two sections, fundamental advances and catalysis and reaction engineering. A distinct feature of this text continues to be the emphasis on molecular chemistry, reaction engineering and modeling to achieve rational and robust industrial design. Our perspective is that this background must be made available to undergraduate, graduate and professionals in an integrated manner.

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