Assessment of the negative factors responsible for the decrease in the enantioselectivity for the ring opening of epoxides catalyzed by chiral supported Cr(III)-salen complexes

Barbara Gigante [a], A. Corma [b], Hermenegildo García [b,*] and María J. Sabater [b]

[a] *INETI, DTIQ Estrada do Paço do Lumiar, 1649-038 Lisboa, Portugal*
[b] *Instituto de Tecnología Química UPV-CSIC, Av. Los Naranjos s/n, 46022 Valencia, Spain*
E-mail: hgarcia@qim.upv.es

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In order to determine the influence of the inorganic support on the asymmetric induction, different chiral chromium(III)-salen complexes have been incorporated within the cavities of zeolites Y, EMT and into the interlamellar region of K-10 montmorillonite. These heterogeneous catalysts are able to promote the asymmetric ring opening of epoxides with trimethylsilylazide to afford chiral azido trimethylsilyl ethers and azido alcohols with modest enantiomeric excess that varies depending on the inorganic support. The factors that have been found to play a negative influence diminishing the enantioselectivity of the supported Cr(III)-salen catalyst compared to the unsupported complexes are the following: (i) the presence of adventitious acid sites, (ii) the encapsulation of no sufficiently stereogenic ligands and (iii) the change in the reaction mechanism from bimetallic to a single metal reaction mechanism.

Keywords: chromium, salen, zeolite, clay, epoxide, azidotrimethylsilyl ether

1. Introduction

Chiral chromium-salen complexes are used for the synthesis of a wide range of useful chiral nitrogenated compounds, which can be versatile synthons in many total syntheses of natural products and drugs [1–6]. Immobilization of chiral chromium-salen complexes on solid supports is desirable considering the potential technological applications of these chromium catalysts in two different types of reactions: C=C double bond epoxidations and epoxide ring aperture. In this regard, recent efforts have been devoted to the immobilization of transition metal complexes in polymers, zeolites and analogous materials in the hope that an activity comparable to solution phase would be accompanied by equivalent or enhanced enantioselectivity [7–13]. Indeed, taking into account that one of the main disadvantages of asymmetric catalysis lies in the cost of the catalysts, the heterogenization of chiral transition metal complexes would constitute a clean and operationally simple way of recycling the active species for re-using or continuous operation. Chief among the examples reported are the incorporation of chiral salen manganese(III) complexes within the cavities of different zeolites, to employ these catalysts in the heterogeneous asymmetric epoxidation of prochiral olefins [14,15]. However, the efficiency of these zeolite-bound complexes in terms of induced enantioselectivity was consistently lower than the results obtained using the same unsupported complexes in homogeneous phase. Among the factors responsible for the decrease of the asymmetric induction, it could be that imperfect preparation procedure and variations in the reaction mechanism or a combination of both could play a major role. Using a different strategy, preformed chiral Co(salen) complexes have been anchored onto the external surface of silica. The resulting solid has shown to be highly selective at low conversions for the kinetic resolution of a racemic mixture of 3,4-epoxy-1-butanol [7].

In the present work chiral chromium(III)-salen complexes supported into zeolitic and layered materials have been obtained and studied as heterogeneous catalysts in the enantioselective ring opening of meso epoxides by azides. The aim of this work is to gain a deeper understanding on the factors that influence the asymmetric induction for the epoxide ring opening using supported chiral salen complexes.

2. Experimental

2.1. Compounds and materials

Starting reagents (salicylaldehyde, *trans*-(R,R)-1,2-cyclohexanediamine, etc.) and reagent grade solvents were purchased from Aldrich and Scharlau, respectively, and they were used without further purification. Pure chromium(III) complexes **1** and **2** were prepared according to literature procedures [16].

Zeolite Y was purchased from PQ zeolites (BET N_2 = 685 m^2/g, A_0 = 2.467 nm, Na_2O = 13.9 wt%, Si/Al = 5.18) and montmorillonite K-10 was supplied by Sud-Chemie in its protonic form and was Na^+ exchanged,

* To whom corespondence should be addressed.

as previously reported in literature [17]. Zeolite EMT was synthesized following the method reported by Davis (Si/Al = 4) [18].

2.2. IR spectra

FT-IR spectra of supported complexes were recorded at room temperature using a greaseless quartz cell fitted with CaF_2 windows in a Nicolet 710 FT spectrophotometer. Self-supported wafers (∼10 mg) were prepared by pressing the zeolite powder at 1 ton cm^{-2}. The samples were outgassed at 100 °C under 10^{-2} Pa for 1 h before recording the IR spectra.

2.3. UV spectra

Room temperature transmission UV-Vis spectra of transparent solutions were recorded in a Shimadzu UV-Vis scanning spectrophotometer. DR spectra of the opaque powders were recorded in a Varian Cary 5G UV-Vis NIR spectrophotometer adapted with a praying mantis attachment and using $BaSO_4$ as reference.

2.4. Preparation of supported complexes

2.4.1. Preparation of ***1-Y***

A mixture of dehydrated Cr^{3+}-pre-exchanged zeolite Y (1 g, 0.65 wt% Cr^{3+}, measured by atomic absorption spectroscopy) and salicylaldehyde (0.37 g, 3.03 mmol) was stirred and refluxed in dichloromethane (10 ml) for 6 h. The organic solution was filtered and the amount of adsorbed salicylaldehyde was calculated by difference between the weight of the residue of the supernatant liquid phase after solvent removal and the initial amount of salicylaldehyde. Then half the stoichiometric amount of the *trans*-(R,R)-1,2-cyclohexanediamine in dichloromethane (10 ml) was added. The resulting yellow slurry was refluxed for 12 h under nitrogen to afford the heterogeneous complex **1-Y**. The sample was filtered, soxhlet extracted in dichloromethane for 8 h to remove excess complex and reactants from the inorganic solid.

2.4.2. Preparation of ***2-EMT***

Similarly to the procedure followed for the preparation of **1-Y**, a mixture of dehydrated Cr^{3+}-pre-exchanged zeolite EMT (1 g, 0.58 wt% Cr^{3+}, measured by atomic absorption spectroscopy) and 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde (0.581 g, 3.03 mmol) synthesized according to a procedure reported by Larrow and Jacobsen was stirred and refluxed in dichloromethane (10 ml) for 6 h [19]. The organic solution was filtered and the amount of adsorbed aldehyde was calculated by difference between the weight of the residue of the supernatant liquid phase after solvent removal and the initial amount of the compound. Then half the stoichiometric amount of the *trans*-(R,R)-1,2-cyclohexanediamine in dichloromethane (10 ml) was added. The resulting yellow slurry was refluxed for 12 h under nitrogen to afford the heterogeneous complex **2-EMT**. The sample was filtered and soxhlet extracted with dichloromethane for 8 h to remove excess complex and reactants from the solid.

2.4.3. Preparation of ***1-K10a***

Synthesis of **1-K10a** was effected by direct anchoring of the complex $\mathbf{1}^+$ to the surface of the clay as follows: a mixture of 8 ml of a solution 1 : 1 acetonitrile–H_2O and 0.141 g (0.3 mmol) of the cationic complex $\mathbf{1}^+$ as perchlorate salt was stirred at room temperature for 24 h. The solid was filtered, soxhlet extracted with acetonitrile and air dried to afford the supported complex **1-K10a**. Preparation of the cationic complex $\mathbf{1}^+$ as perchlorate salt was accomplished starting from the (R,R)-Cr(salchd) chloride complex as follows: a 100 ml round-bottom flask fitted with a dropping funnel was charged with 1.09 g (5.25 mmol) of $AgClO_4$ and 15 ml of CH_3CN. The dropping funnel was charged with a solution of 2.35 g (5 mmol) of (R,R)-Cr(III)(salchd)Cl complex in 10 ml of CH_3CN and this solution was added dropwise. The mixture was stirred 24 h and then filtered through Celite. The filtrate was concentrated to dryness to give complex $\mathbf{1}^+$ as perchlorate salt. IR(KBr): 2956, 2868, 1631, 1542, 1447, 1147, 1110, 1090 and 621 cm^{-1}; UV-Vis (CH_2Cl_2): 230, 285, 320, 365 and 420 nm; MS(FAB): $m/z = 372$ $(M–ClO_4)^+$.

2.4.4. Preparation of ***1-K10b***

Synthesis of **1-K10b** was basically as described for complexes **1-Y** and **2-EMT**. Hence a mixture of dehydrated Cr^{3+}-pre-exchanged montmorillonite K-10 (1 g, ion-exchange capacity: 10 meq/100 g) and salicylaldehyde (0.37 g, 3.03 mmol) was stirred and refluxed in dichloromethane (10 ml) for 6 h. The organic solution was filtered to calculate the amount of adsorbed salicylaldehyde. Then half the stoichiometric amount of chiral *trans*-(RR)-1,2-cyclohexanediamine in dichloromethane (10 ml) was added. The resulting yellow slurry was refluxed for 12 h under nitrogen, filtered and soxhlet extracted with dichloromethane to afford the heterogeneous complex **1-K10b**.

2.5. General procedure for the ring-opening reactions

For the reactions with the homogeneous catalysts a similar procedure as that described by Jacobsen was followed [16]. Thus, a 10 ml Schlenk tube was charged with 0.3 mmol of catalyst and 1 ml of diethyl ether. The epoxide (3 mmol) was added and the mixture was stirred for 15 min and then 3.15 mmol of $TMSN_3$ was added. The resulting brown solution was stirred at room temperature under nitrogen atmosphere for the time indicated in table 1. The solution was filtered through silica gel and the resulting filtrate was analyzed by GC (Chiraldex G-TA column). For the heterogenized catalysts a similar procedure was followed: 105 mg of supported complex was suspended in dry ether (1 ml) followed by the addition of the epoxide (3 mmol) and the suspension stirred for 15 min. Then, azidotrimethylsi-

Table 1
Enantioselective ring opening of epoxides with $TMSN_3$ catalyzed by chromium (salen) complexes.[a]

Catalyst	Substrate	Conversion[b] (%)	Time (h)	Reaction products[b] (%)			ee[b,c] (%)
				Azido silyl ether	Azido alcohol	Other[d]	
1	**4**	94	20	79	17	4	22
1-Y	**4**	100	120	61	21	18	8
1-K10a	**4**	80	70	26	31	43	3
1-K10b	**4**	73	70	40	14	46	4
2	**4**	94	19	76	18	6	68
2-EMT	**4**	65	120	24	75	1	16
1	**5**	95	28	61	25	14	18
1-Y	**5**	100	120	43	29	28	10

[a] All reactions were performed at room temperature with 3 mmol of epoxide, 0.3 mmol of unsupported catalyst or 0.105 g of heterogeneous complex and 3.15 mmol of $TMSN_3$ in 1 ml of Et_2O.
[b] Determined by chiral capillary GC (Chiraldex G-TA, 30 m × 25 mm).
[c] Enantiomeric excess of azido silyl ether.
[d] Diols and non-identified products.

lane (3.15 mmol) was added. The resulting suspension was stirred at room temperature and the enantiomeric composition followed by GC analysis (Chiraldex G-TA column).

3. Results and discussion

Encapsulation of (R,R)-Cr(III)salchd complex (R,R)-**1** (salchd = 1,2-bis(salicylidenimino)cyclohexane) within the cavities of zeolite Y was carried out in a stepwise procedure by forming the ligand from one diamine molecule *trans*-(R,R)-(1,2-cyclohexanediamine) and two molecules of salicylaldehyde in the presence of templating Cr^{3+} ions resident in pre-exchanged zeolite Y (0.65% weight Cr^{3+}, 1 Cr^{3+} every 5 supercages) (see scheme 1). The sample was soxhlet extracted with dichloromethane to remove the excess of ligand and reactants from the inorganic solid, affording the heterogeneous complex **1-Y**.

Characterization of **1-Y** by IR spectroscopy showed the characteristic IR vibration bands at 1615 and 1535 cm^{-1} that have been proposed as specific of pure unsupported Cr(III)-salen complexes. Thus, figure 1(d) shows that the sample **1-Y** exhibits an imine stretching vibration around 1615 cm^{-1} and the typical band of metallosalen complexes at 1535 cm^{-1} (figure 1). On the other hand, the diffuse reflectance spectrum of **1-Y** was similar to the UV-Vis spectrum of the corresponding unsupported complex in solution although the characteristic metal-to-ligand band at ca. 350 nm undergoes a solvatochromic shift of ca. 50 nm

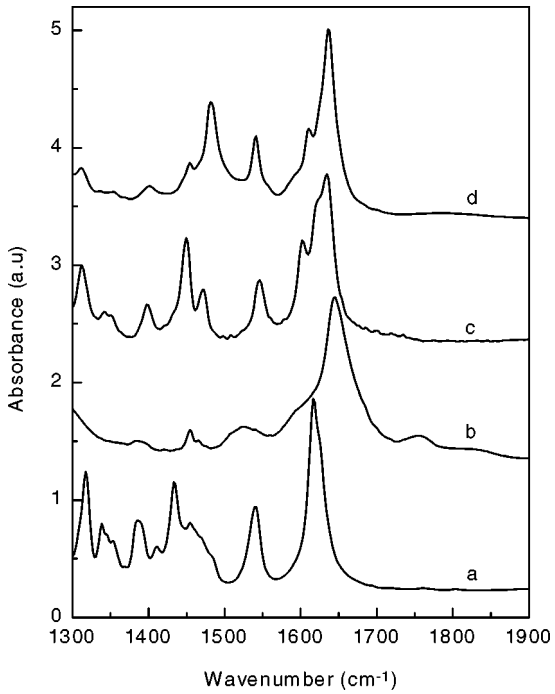
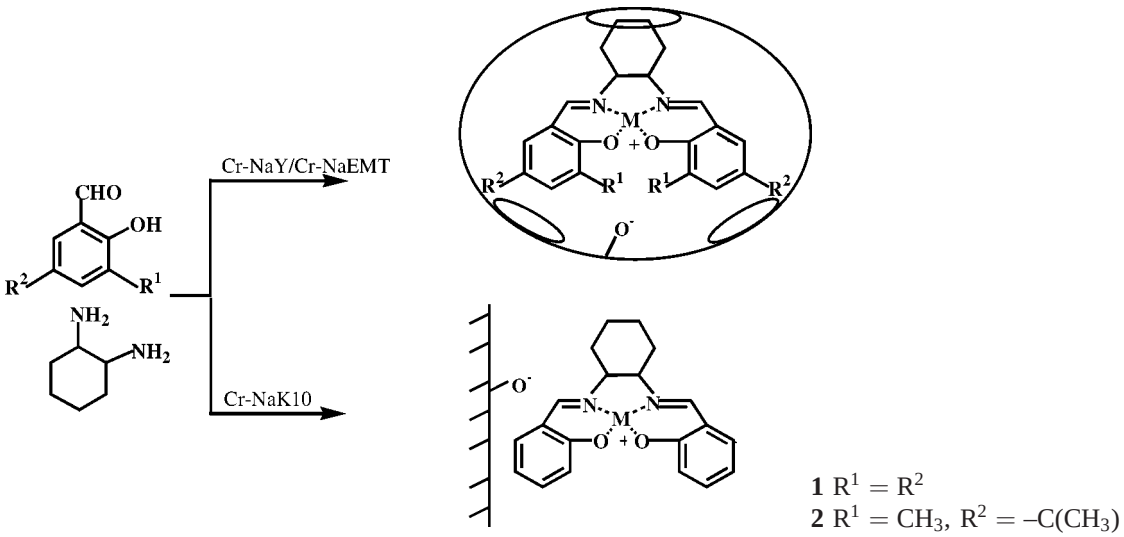


Figure 1. IR spectra of complexes **2** (KBr) (a), **2-EMT** (b), **1** (KBr) (c) and **1-Y** (d), respectively. The IR spectra of the supported complexes have been recorded at room temperature after heating at 200 °C while outgassing at 10^{-5} mbar for 1 h.



Scheme 1. Preparation of chromium(III) Schiff base complexes into the cavities of zeolites Y, EMT and in the montmorillonite clay K-10.

when complex **1** is encapsulated inside zeolite Y (figure 2).

Analogously, two samples of the complex (R,R)-**1** incorporated in the interlamellar region of a layered clay (montmorillonite K-10) were prepared by different incorporation procedures. In the first one, preformed $\mathbf{1}^+$ as ClO_4^- salt was directly ion exchanged into K-10 to obtain **1-K10a**. In the second one, the preparation of chromium complex (R,R)-**1** was carried out by heating at reflux temperature a suspension of salicylaldehyde and dehydrated Cr^{3+} pre-exchanged montmorillonite K-10 (1.14 wt% Cr^{3+}) in dichloromethane for 4 h; after filtering, the solid was added to a solution of *trans*-(R,R)-1,2-cyclohexanediamine and the resulting suspension was refluxed additionally for 12 h to afford the heterogeneous complex **1-K10b** (scheme 1). The two solids were soxhlet extracted with dichloromethane and characterized by IR and DR spectroscopy. As in the case of **1-Y**, the IR and the electronic absorption spectra of the supported complex **1-K10b** resemble closely those obtained for the pure chromium complex **1** synthesized independently according to previously described methods (see figure 2 for the DR spectrum) [16]. Therefore, from the spectroscopic point of view, no differences in the efficiency of these solids as catalysts for the asymmetric induction should be expected.

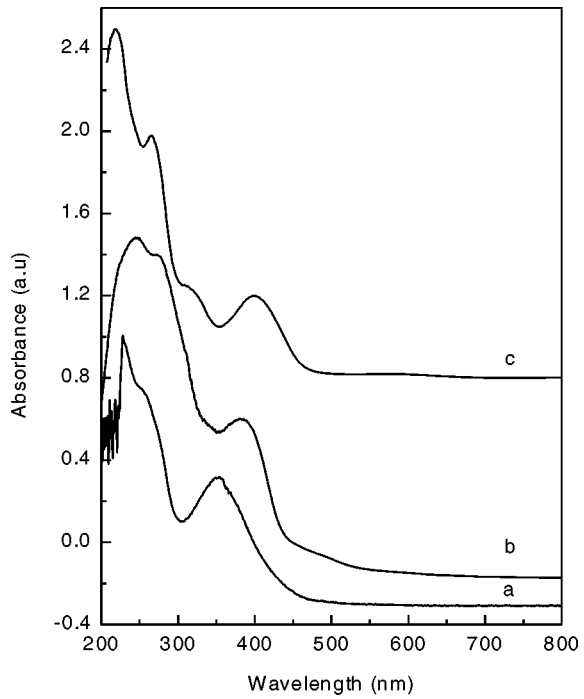
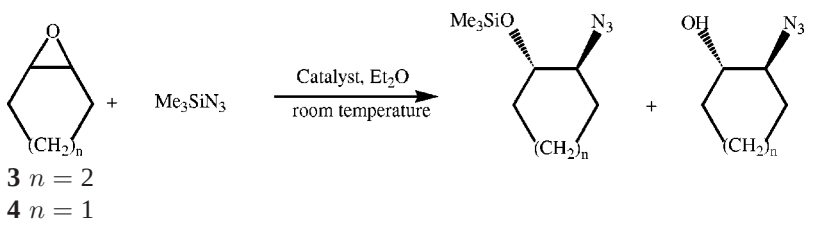


Figure 2. UV-Vis of pure complex **1** (10^{-4} M) in dichloromethane (a) and DR spectra plotted as the inverse of the reflectance (R) of the supported complexes **1-K10b** (b) and **1-Y** (c), respectively.

Unsupported salen complexes having ligands substituted with bulky alkyl groups such as chromium(III)-(RR)-1,2-bis [(3-*tert*-butyl-5-methyl-salicylidenimino)]cyclohexane (**2**) have been found in solution to induce higher enantiomeric excesses than the chiral complex of the unsubstituted salchd ligand. Aimed at comparing the perfomance of **1-Y** and **1-K10** with a zeolite-bound complex having bulkier ligand, the complex **2** was also prepared.

Given the larger size of complex **2** compared to **1**, zeolite EMT instead of Y was chosen as host. Zeolite EMT is the hexagonal form of the well-known faujasite structure (unit cell: two hypercages with an internal diameter of 1.3×1.4 nm and about 1.2 nm^3 void volume and two hypocages with 1.2 nm diameter and 0.6 nm^3 void volume) [18]. The assembly of this bulky chromium complex was accomplished into the EMT zeolite cages by means of a stepwise inclusion procedure similar to that described for complex **1-Y**. Thus, the intrazeolite condensation of *trans*-(R,R)-(1,2-cyclohexanediamine) and 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde was carried out in the presence of a Cr^{3+}-pre-exchanged zeolite EMT (0.58% Cr^{3+}, 1 Cr^{3+} every 5 supercages) following the procedure previously reported in the literature for related chiral Mn(III)-salen complex [14]. The mixture was heated at reflux in dichloromethane for 4 h (scheme 1). After filtering and soxhlet extraction, the successful formation of supported complex **2-EMT** was confirmed by IR and DR spectroscopy. Figure 1 provides a comparison of the IR spectra of **2-EMT** with an authentic sample of the unsupported complex **2**. We noticed that the IR bands of the unsupported complex are in general sharper and better resolved while those of sample **2-EMT** are broader. However, for identification purposes the two specific metallosalen bands at ca. 1615 and 1535 cm^{-1} are still observed in the spectrum of figure 1(b).

In order to assess the influence of complex immobilization we compared the perfomance of the zeolite-bound complexes, not with the Jacobsen catalyst containing *tert*-butyl groups on the aromatic ring, but exactly with the same complexes **1** and **2** without any support. Hence, the catalytic activity of these materials was evaluated on the ring-opening reaction of cyclohexane oxide **3** and cyclopentane oxide **4** by trimethylsilylazide ($TMSN_3$) to produce mainly the corresponding azido trimethylsilyl ethers accompanied with minor amounts of azido alcohols (scheme 2). As



3 $n = 2$
4 $n = 1$

Scheme 2. Enantioselective ring opening of cyclic oxides **3** and **4** by Me_3SiN_3 catalyzed by chiral chromium Schiff base complexes.

can be seen in table 1, total conversions were achieved with the supported catalyst **1-Y**, while comparatively lower ones were obtained with **1-K10** and **2-EMT**. However, the reaction times required for the heterogeneously catalyzed reaction are remarkably longer than those needed with homogeneous catalysts. Traditionally, this has been attributed to restrictions imposed to the diffusion of reactants and products through the micropores of the zeolite lattice as compared to unrestricted diffusion in solution.

The most salient data from table 1 is that the enantioselectivity of the ring-opened azide has been largely reduced with respect to that achieved with the unsupported complexes in homogeneous phase. In addition to this, the enantioselectivity appears to vary depending on the complex (**1** vs. **2**) and the nature of the host (Y, EMT, K-10). In this regard, it is worth noting that most of the related precedents comparing the enantioselectivity of Schiff base complexes supported on inorganic solids with that attained in homogeneous solution for C=C epoxidation report a remarkable decrease on the enantioselectivity upon heterogenization [11b,11d,14]. Although C=C double bond epoxidation has a reaction mechanism different from epoxide ring aperture, they have in common the metallo-salen catalyst. It is of importance to understand the origin of this loss of enantioselectivity upon incorporation of the active complex in the aluminosilicate supports, because this understanding will contribute to obtain more selective heterogeneous catalysts.

Given that asymmetric induction producing in a certain selectivity one of the two possible enantiomers, arises from the discrimination between two reaction pathways having very similar activation energies, several reasons can be advanced to explain the reduction of the enantioselectivity [20]. First, it could happen that besides Cr(III)-salchd adventitious sites of the aluminosilicate framework and/or uncomplexed Cr^{3+} ions could also participate in the catalysis providing unselective parallel pathways. To address this point, blank runs using the supposedly inert hosts were carried out. These controls explain why the clay-supported complexes **1-K10a** and **1-K10b** behaved much less selectively towards the formation of the azido trimethylsilyl ether and azido alcohol as compared with its intrazeolite analog (table 1). Thus, control experiments with the original Na^{+}-pre-exchanged montmorillonite (NaK10 was prepared from commercial montmorillonite K-10 in its protonic form) and Na-Y zeolite revealed that the former was able to catalyze the ring-opening reaction of the epoxide to afford significant amounts of diol as by-product. By contrast, this secondary reaction was not detected in the case of the original NaY zeolite. This experimental fact evidences the existence of certain Lewis and/or Brønsted acidity in the original clay. In addition to this, control experiments with the chromium-exchanged materials (Cr-Y, Cr-EMT and Cr-K10) confirmed that Lewis acid activation of the epoxide by the existence of residual uncomplexed chromium is a secondary reaction of major importance in the case of the clay, playing only a minor role in Cr-Y and Cr-EMT.

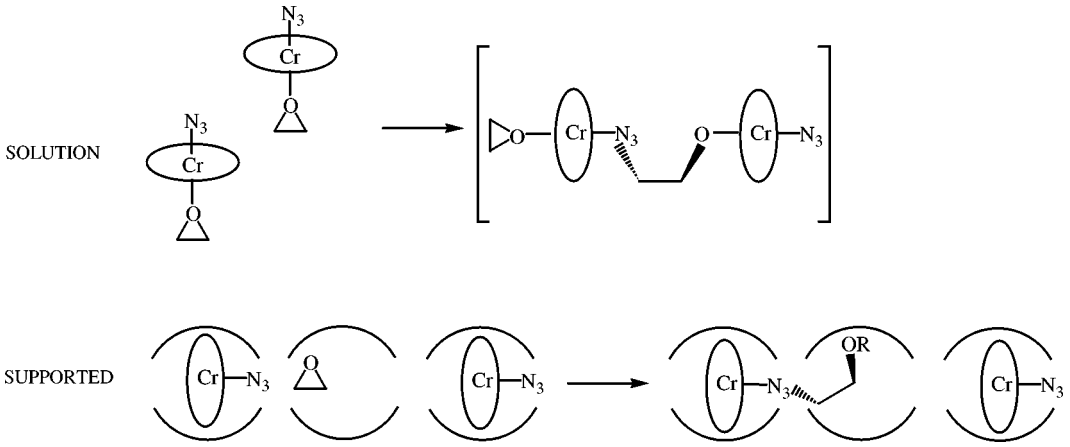
A second factor that can contribute to the reduction of enantioselectivity in the heterogeneous catalyzed reaction is the fact that the ship-in-a-bottle synthesis of the complexes does not lead to pure enough complexes. For non-supported Cr^{3+}-salen complexes, purification before their use as catalysts can be done by recrystallization in appropriate solvents, but purification is obviously not possible for the encapsulated complex apart of solid–liquid extraction.

To address this point, the preformed $\mathbf{1}^{+}$ complex was directly ion exchanged into the interlamellar regions of montmorillonite K-10. The layered structure of K-10 clay makes possible in this case the incorporation of bulky large positively charged complexes that are size excluded for zeolites Y and EMT. Comparison of the results achieved using supported complex **1** in montmorillonite incorporated by ion exchange (**1-K10a**) or by ship-in-a-bottle synthesis (**1-K10b**) reveals that the reduction of the enantiomeric excess cannot be attributed solely to the ship-in-a-bottle synthesis of the ligands around resident Cr^{3+}; although it is obvious that the fact that supported complexes cannot be purified inside the support and require extremely efficient synthesis is a disadvantage with respect to the homogeneous complexes. This would explain why strategies based on the anchoring of pure metal salen complexes have reported to lead to higher enantiomeric excesses for the hydrolytic epoxide ring opening at low epoxide conversions [7].

A third factor to be considered is the fact that an efficient asymmetric induction requires bulky ligands around the active Cr^{3+} ion in order to create a stereogenic environment. This is well established for unsupported complexes. However, when these complexes are going to be encapsulated inside the supercages of zeolites, a compromise with the size of the substituents on the stereogenic ligand has to be reached since otherwise the molecular size of the complex will be too large to be accommodated inside the cages. An ideal situation would be to find a host whose dimensions exactly match those of the enantioselective catalyst. Unfortunately this is not always possible and the fit of the catalyst normally requires the selection of appropriate substituents even though the enantioselectivity of the system could be decreased. This is clearly seen in table 1, wherein catalyst **1** has a lower performance than **2**. A reflection of this is the fact that **1-Y** exhibits a poorer enantioselectivity than **2-EMT**.

Finally, another factor to be considered is the possibility of changes in the reaction mechanism of the enantioselective reaction from the unsupported to the supported catalyst.

Concerning the influence of encapsulation on the mechanism of the Cr(III)-salen-catalyzed epoxide ring aperture, it has been reported that there is a second-order kinetic dependence on the catalyst (scheme 3) [21]. It is obvious that the participation of two encapsulated complexes in the heterogeneous catalyst is not possible or much less likely since they are immobilized in isolated supercages. Therefore, presumably the molecularity of the catalytic epoxide aperture in the case of encapsulated complexes has to be first order with respect to the complex. This change in



Scheme 3. Proposed operating reaction mechanisms of Cr-catalyzed ring opening of epoxides: bimetallic in solution and monometallic when supported.

the molecularity of the catalytic process from second order (unsupported complexes) to first order (supported complexes) can result not only in a decrease in the reaction rate of the catalyzed ring opening but also in a remarkable decrease of the enantioselectivity of the process, as it is in fact observed. Indeed, it has been demonstrated that Cr(III)-salen-catalyzed ring opening of epoxides involves catalyst activation of both nucleophile and electrophile in a bimetallic rate-determining step (scheme 3) [21]. Accordingly, it has been observed that the bimolecular rate constant is largely increased by linking the catalysts units in a determined dimeric form. In fact, this specific covalent linkage has provided catalysts one to two orders of magnitude more active and enantioselective than the monomeric analogs [22]. This implies that the proximity between two catalytic centers and the convenience that these metal centers achieve an optimal geometry in the rate-determining transition state exert a crucial influence in the activity and enantioselectivity of chromium(salchd) catalysts.

Thus, the significant loss of enantioselectivity observed in table 1 for the supported Cr(salchd) complex can be explained if we take into account that in solution the epoxide ring-opening mechanism proceeds through a simultaneous activation of both the nucleophile and the electrophile by two catalyst molecules in a bimetallic enantioselective determining step [21]. Participation of the chiral salen complexes creates a remarkable asymmetric environment during the attack of the azide to the epoxide. Since each supercage can accommodate a single complex, the two metal centers will be separated by a considerably long distance and a simultaneous bimetallic activation by two chromium complexes will not be possible in the intrazeolite mechanism. Accordingly, we propose that for the zeolite-bound Cr(salchd) catalyst the active species is the azide complex Cr(III)salenN_3 formed initially from the starting complexes **1-Y** and **2-EMT**, whereas activation of the epoxide either does not take place or is effected by adventitious Lewis sites placed in the same supercage. Participation of a single chiral complex should produce a less pronounced asymmetric environment than two interacting chiral complexes as is the case of homogeneous phase. In addition there will be an optimal selective determining transition state that obviously cannot be achieved when the complexes are site isolated in the supercages of the zeolite. This circumstance would explain that the intrazeolite transition state is less enantiodiscriminating than that attained in homogeneous phase. Similarly, the poor enantiomeric excesses obtained in the case of clay-supported complex might be related to the predominance of the non-selective ring-opening route in this solid due to a major content of Lewis and/or Brønsted centers. In fact, the highest enantiomeric excesses in azido trimethylsilyl ether were achieved with the intrazeolite complexes **1-Y** and **2-EMT**.

4. Conclusions

Aimed at determining the influence of encapsulation within zeolites on the enantioselectivity of chiral Cr(salchd) complexes, two complexes have been immobilized into the cavities of zeolites Y and EMT by a stepwise synthesis. A similar sequential procedure has been employed to incorporate a chiral chromium-salen catalyst into the interlamellar swelling spaces of a smectite clay.

These supported complexes have shown a variable activity as catalysts in the asymmetric ring opening of cyclic oxides with $TMSN_3$ to afford the respective azido trimethylsilyl ethers and minor amounts of azido alcohols. In general the heterogeneous complexes are less reactive and enantioselective than the corresponding homogeneous analogs. This has been attributed to a series of factors that require to be addressed before optimum zeolite-bound enantioselective catalysts can be devised. Among them, we have shown the following to play a negative influence: (i) the presence of adventitious acid sites, (ii) the encapsulation of no sufficiently stereogenic bulky ligands in large zeolite cages and (iii) changes in the operating reaction mechanism.

Thus, the intrazeolite isolation of the complex or in general immobilization of guest molecules on solid supports that usually prevents undesired bimolecular aggregation reactions, is paradoxically likely in this case to be a disadvan-

tage to attain highly reactive and enantioselective chromium catalysts.

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