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Cr^{III}(salen) impregnated on silica for asymmetric ring opening reactions and its recovery via desorption/re-impregnation

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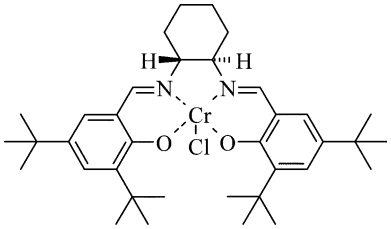
Abstract—The impregnation of Cr^{III}(salen) complexes on silica resulted in a heterogeneous catalyst for the asymmetric ring opening (ARO) reaction of epoxides with good selectivity and acceptable activity. As became apparent from a series of 10 successive batch tests in the ARO reaction of 1,2-epoxyhexane, leaching was limited, while catalytic activity and selectivity were acceptable. Though the support suffered from abrasion in the batch reactor, 80% of the catalyst was easily recoverable via simple extraction from the used solid catalyst and entirely transferable onto a fresh carrier via impregnation. It was shown that 80% of the leached catalyst at the end of the tests could be transformed into a fresh heterogeneous catalyst as well.

The few reported attempts to immobilise a Cr^{III}(salen) complex (Fig. 1) onto support materials have involved coordination, chemical tethering and encapsulation.[1–5] For asymmetric ring opening (ARO) reactions of epoxides,[1] the complexes immobilised through coordination suffered from significant leaching.[2] The relative weakness of the coordination bond which anchors the metal to the functionalised support, in a single run, caused 20–45% leaching of the complex from the solid into solution because of the occurrence of ligand exchange processes during the reaction. Whereas the catalysts chemically bonded via ligand tethering resulted in catalytic systems with little or no leaching, the reduced activity and selectivity were drawbacks.[2,3] Possibly the density of the chromium complex was too low and consequently the mechanistically required cooperative effect[4] resulting from the participation of two neighboring catalyst molecules in the reaction mechanism was absent.



(*R*,*R*)-**1**

Figure 1. The Cr^{III}(salen)-complex.

The encapsulation of the Cr^{III}(salen) complex inside large pores of zeolites Y and EMT, or within K-10 montmorillonite, experienced a lowering of the asymmetric induction ability of the supported catalyst.[5] The presence of Brönsted acid sites and the lack of bulky stereogenic groups on the encapsulated ligands used possibly account for the reduced reactivity and selectivity.

The chemical tethering of the complex via a covalent bond between support and ligand requires the ligand synthesis strategy to be redesigned as was shown for Co(salen) on MCM-41,[6] silica[7] and polymers.[7] The procedure is expensive and time consuming, while regeneration of the resulting catalyst at best requires subtle procedures. Minor changes in the steric environment of the transition metal by tethering the ligand to a solid surface may alter the enantioselective discrimination power of the catalyst.[3]

In this perspective the cheap, easy and fast immobilisation of the 'homogeneous' complex **1** by impregnation on a silica[8] support was investigated. Judicious selection of solvents, not only allowed the use of silica physisorbed (*R*,*R*)-Cr^{III}(salen) complex in ARO reactions in conditions devoid of significant leaching, but also its desorption from contaminated support and re-adsorption on fresh carrier. Since the Cr(salen) com-

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plex is insoluble in noncoordinating solvents but readily soluble in donor solvents such as ethereal solvents,[9] diethyl ether and hexane were used as solvent during the catalyst impregnation and ARO reaction, respectively. Complex removal from a used catalyst was done in tetrahydrofuran (THF) (in a Soxhlet extractor).

Typically, portions of a solution of 0.2 mmol of the (*R*,*R*)-Cr^{III}(salen) catalyst (bought from Strem Chemicals) in 50 ml diethyl ether were impregnated on 10 gram of dry silica. The impregnated silica containing 20 μmol catalyst/gram silica[10] was dried overnight at 60°C.

To assess the catalytic performance of the immobilised Cr(salen) complex, the impregnated silica material was used in batch experiments. In Figure 2, the enantiomeric or diastereomeric excess (e.e./d.e.)[11] and conversion percentages are given for a range of epoxide substrates. The kinetic resolution of the terminal epoxides (1,2-epoxyhexane and 1,2-epoxyoctane) resulted in very high e.e. values (>97.5%) at conversions of about 50%.

For other substrates like styrene oxide and the meso-epoxides cyclohexene oxide and cyclopentene oxide, the ARO displayed lower selectivities. Remarkable is the good selectivity achieved for the kinetic resolution of (+)- and (−)-limonene-1,2-epoxide.[12] Diastereomeric excesses of 80–90% were obtained at conversions varying from 48 to 65%.

The impregnated silica with a Cr(salen)-catalyst loading of 1.25 wt% was further tested in an epoxyhexane ARO recycling experiment using the conditions described above. For 10 consecutive ARO reactions of epoxyhexane, a 3 mol% catalyst/substrate ratio was used and a slight excess of 0.6 equiv. of $TMSN_3$. After each batch

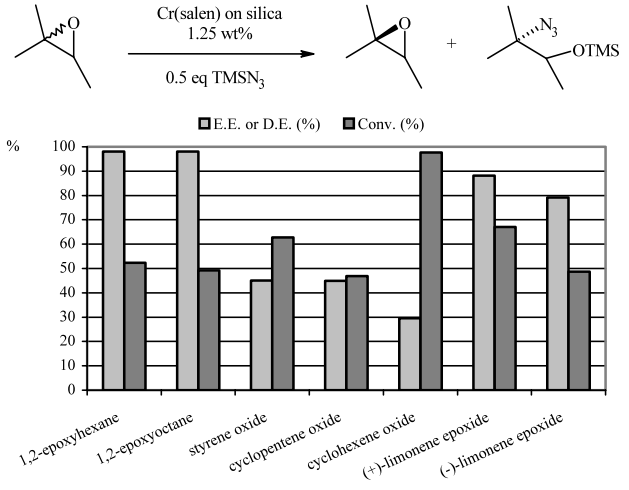


Figure 2. Substrate screening for an ARO reaction at 295 K after 25 h with silica impregnated (*R*,*R*)-Cr^{III}(salen) (20 μmol catalyst/gram silica) using a catalyst/substrate ratio of 3 mol%, a substrate/solvent ratio of 0.2 vol% and added toluene as internal standard. The optimum conversion is 100% for cyclohexene and cyclopentene epoxide; for the other substrates it is 50%.

experiment, the solid catalyst was removed from the reaction mixture by sedimentation–filtration. After every run, the concentration of the complex in solution was determined by UV–Vis absorption spectroscopy at 430 nm[13] in a 50/50 volume mixture of hexane and diethyl ether, allowing the determination of concentrations of the complex of 0.1 ppm. The conversion and enantioselectivities do not deteriorate during successive tests, while the low degree of leached complex cannot be responsible for a contribution to the activity.[14] The initially high leaching can be eliminated with a catalyst with reduced loading of the complex.

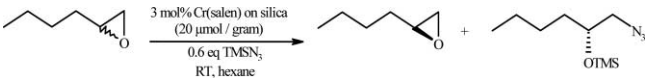
During the recycling experiment, 1,2-epoxyhexane was obtained with an enantiomeric excess ranging from 82 to 93%, whereas the e.e. values for the azido trimethylsilyl ether (not listed in Table 1) varied from 60 to 71%.

During the successive tests, deterioration of the silica support seems to occur, as a result of the severe abrasive forces in the stirred reactor. Whereas continuous fragmentation of the silica carrier has only a minor impact on the reaction kinetics, the time needed for the recuperation of the heterogeneous catalyst by sedimentation/centrifugation increases steadily. The enhanced leaching at the (9th and) 10th cycle is assumed to be the result of this fragmentation.

Recovery of the Cr(salen) catalyst from fragmented silica particles could be done by a Soxhlet extraction in THF. To avoid the issue of the deterioration of the silica, the possible recovering of the catalyst by means of a desorption procedure was investigated. The objective would be to desorb the complex before the silica material reaches a certain level of degradation, and to reuse the desorbed catalyst to impregnate a new batch of silica.

The Cr(salen) on silica catalyst recovered after the 10th run was subjected to a Soxhlet extraction with THF for

Table 1. Recycling experiments with Cr(salen) impregnated silica catalyst in the ARO reaction of epoxyhexane



Run	Time (h)	E.e.[a] (%)	Conversion[b] (%)	Leaching (%)
1	21	84.9	53.3	0.59
2	21	87.2	46.3	1.83
3	23	91.5	48.4	1.07
4	23	91.6	53.4	0.17
5	23	92.8	55.6	<0.01
6	23	92.9	52.8	0.01
7	24	90.9	50.2	0.08
8	26	82.3	51.4	<0.01
9	33	84.9	50.9	0.30
10	41	86.2	50.8	1.22

[a] Enantiomeric excess of (*R*)-1,2-epoxyhexane.
[b] The optimum conversion should be 50%.

12 h. As determined by UV–Vis spectroscopy, almost 80% of the Cr(salen) remaining on the silica surface was recoverable. The retrieved catalyst was tested for its catalytic performance, and exhibited identical reactivity and selectivity compared to the fresh catalyst. The 20% residual complex remaining on the silica after desorption was found to be inactive. Although the true origin of this effect is being examined, and its carrier dependence is being investigated, it is not impossible that due to the high dilution degree of the residual complex at the surface, the mechanistically required cooperative effect disappears. Alternatively, preliminary ESR results show good resemblance with a Cr-on-silica polymerisation catalyst.

The small amount of leached Cr(salen) catalyst is recoverable as well and can be re-impregnated on a fresh support. During work-up of the enantioenriched epoxide and ring opened products, the catalyst can be separated by an extraction.[15] Hence, the total of recoverable catalyst amounts to $\sim$80%.

Acknowledgements

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8. Silica gel 60 for preparative column chromatography was bought from Fluka.
9. A catalyst/silica ratio of 1.25 wt%, corresponding to 20 μmol/gram, showed optimal performance. Based on a screening experiment in which a range of catalyst loadings were tested, this sample combined low leaching degrees with good enantioselectivity. Higher catalyst/silica ratios of 2.5, 5.0 and 10 wt% suffered from leaching varying between 5 and 30%.
10. Hansen, K. B.; Leighton, J. L.; Jacobsen, E. N. *J. Org. Chem. Soc.* **1996**, *118*, 10924–10925.
11. All enantiomeric/diastereomeric excesses were determined by chiral GC on a Chrompack-CHIRASIL-DEX CB column (0.32 mm×0.25 μm×25 m) using FID detection.
12. Dioos, B. M. L.; Jacobs, P. A. *Tetrahedron Lett.* **2003**, *44*, 4715–4717.
13. Cr^{3+} ions have two absorption bands at about 430 and 614 nm due to d–d transitions.
14. In an homogeneous reference experiment with 375 ppm of Cr(salen) carried out in hexane, the conversion and e.e. after 24 h was 25 and 26%, respectively. Consequently, under the conditions described in Table 1, the amount of complex corresponding to a degree of leaching of 1% should not contribute significantly to the conversion.
15. During solvent evaporation the catalyst precipitates, while both epoxide and ring opened products can be extracted in hexane, in which the catalyst-precipitate will not dissolve.