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Journal of Catalysis 243 (2006) 217–219

JOURNAL OF CATALYSIS

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Priority Communication

Heterogenisation of dimeric Cr(salen) with supported ionic liquids

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Received 21 June 2006; revised 14 July 2006; accepted 18 July 2006

Abstract

A dimeric Cr(salen) catalyst was successfully immobilised in a silica-supported ionic liquid. The heterogeneous catalyst offers very high selectivity and good reactivity for asymmetric ring-opening reactions of epoxides. It can be used in a continuous-flow reactor as an alternative for the homogeneous reaction.

Keywords: Ionic liquid; Cr(salen); Heterogenisation; Asymmetric ring opening; Epoxides

1. Introduction

The chiral Cr(salen) complex (**1**) is an effective and highly selective catalyst for the asymmetric ring-opening (ARO) reactions of epoxides (Fig. 1) [1]. Because this transition metal complex is expensive, catalyst recycling is mandatory. This can be done by traditional separation techniques, such as distillation; however, this is not without risk, because organic and metal azides are present in the reaction mixture. These problems can be avoided by immobilising the Cr(salen) complex and using it as a heterogeneous catalyst. Thus far, several heterogenisation strategies have been described for the Cr^{III}(salen) catalyst.

Catalysts chemically bound to inorganic supports through ligand tethering result in catalytic systems with little or no leaching, but with reduced activity and selectivity as major drawbacks [2]. A polymer-supported Cr(salen) catalyst also suffers from low leaching, necessitating a redesign of the ligand. The resulting changes in the steric environment of the transition metal reduces the enantioselective discrimination potential of the catalyst [3]. Encapsulation of the complex in the large pores of zeolites results in decreased asymmetric induction ability of the supported complex and loss of the cooperative catalytic effect [4]. Although the complexes immobilised by coordination offer acceptable enantioselectivities, they suffer from moderate leaching in the resolution of *meso*-epoxides [5]. The Cr(salen) complex impregnated on silica offers good enantioselectivity for the ARO of terminal epoxides and suffers from low leaching degrees [6], with the leaching further reduced by the synthesis of a dimeric Cr(salen) catalyst (**2**) [7].

Ionic liquids have received much attention over the last decade, and their applications as green solvents in catalysis have been described [8,9]. A relatively new approach involves using supported ionic liquid phases to immobilise homogeneous catalysts [10,11]. One important advantage of supported ionic liquid phases over biphasic reaction systems is that biphasic systems always require larger amounts of ionic liquid. Therefore, as an alternative to the impregnation technique, the application of a supported ionic liquid phase was investigated for the immobilisation of a homogeneous Cr(salen) catalyst.

2. Experimental

In this framework, the commercially available [BMIM][PF_6] was used because it offers higher enantioselectivities for the ARO reaction than other 1-butyl-3-methyl-imidazolium salts. In fact, catalyst activity and selectivity are strongly influenced by the nature of anion present in the ionic liquid [12]. For the catalytic tests, 1,2-epoxyhexane and cyclohexene oxide were chosen as representative substrates for the two major substrate classes (i.e., terminal epoxides and *meso*-epoxides).

The heterogeneous catalyst was prepared by dissolving the dimeric Cr(salen) catalyst (**2**) together with the [BMIM][PF_6]

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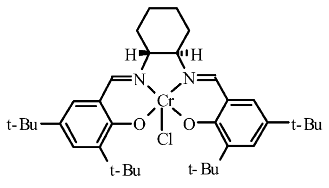
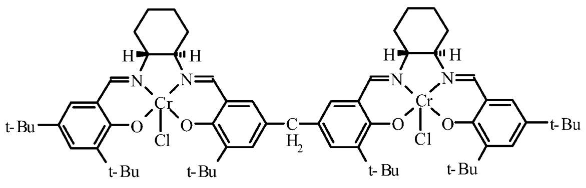
doi:10.1016/j.jcat.2006.07.017



1



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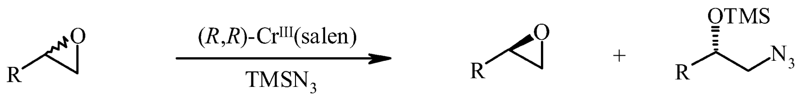
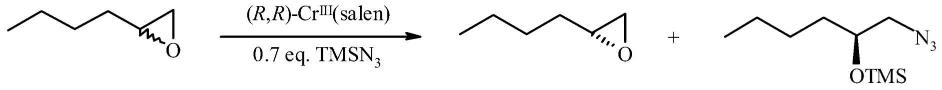


Fig. 1. ARO of epoxides catalysed by (R,R)-Cr^{III}(salen) complexes.

Table 1
Stirred batch reactor: ARO of epoxides catalysed by a dimeric (R,R)-Cr^{III}(salen) complex immobilised in a supported ionic liquid phase compared to the dimeric complex impregnated on silica and the reported homogeneous reactions with the monomeric Cr(salen) complex

a



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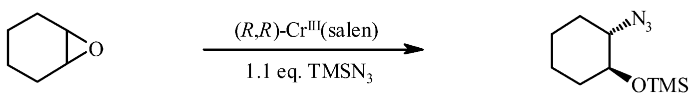


Run[a]	Reaction	Time (h)	Conversion (%)	EE epoxide (%)	EE product (%)	Leaching (%)
1	a	3	52	95	84	0.4
2	a	3	48	96	87	0.5
3	b	20	93	–	75	1.1
4	b	20	92	–	73	1.1
Impregnation[b]	a	10	59	96	66	1.0
Impregnation[b]	b	70	98	–	65	1.1
Homogeneous[c]	a	27	45	–	97	–
Homogeneous[d]	b	18	83	–	84	–

Note. The catalyst/substrate ratio is 1.5 mol% for the supported ionic liquid phase (SILP) catalyst, 3 mol% for the impregnated catalyst and 2 mol% for the homogeneous reaction.

[a] Runs 1–4 are consecutive experiments with the same catalyst in a stirred batch reactor.

[b] Dimeric Cr(salen) catalyst impregnated on silica, data from Ref. [7].

[c] Homogeneous reaction at 0–2 °C, optimised for product selectivity, data from Ref. [13].

[d] Homogeneous reaction at room temperature, optimised for product selectivity, data from Ref. [14].

ionic liquid in acetone. After addition of the silica support material, the resulting suspension was stirred open to air until all solvent was evaporated.

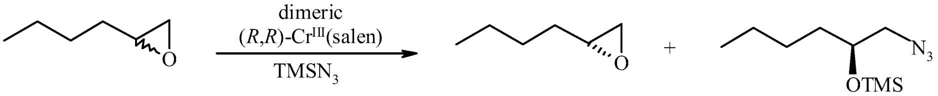
The reactions were performed at room temperature in a stirred batch reactor (glass vial) and a glass U-tube for the continuous-flow experiment, using hexane as solvent and octane as internal standard. The reaction mixture was analysed by a chiral gas chromatograph, equipped with a Chrompack-CHIRASILDEX CB column (0.32 mm × 0.25 mm × 25 m) with flame ionisation detection. The complex concentrations in solution were determined by UV–vis absorption measurements.

3. Results and discussion

Compared with the impregnated dimeric complex [7], the use of a supported ionic liquid phase (SILP) to immobilise the dimeric Cr(salen) catalyst offers several benefits (Table 1). First, increased reactivity was observed: a TOF of 11.5 h^{-1} for the SILP immobilisation, compared with a TOF of 1.9 h^{-1} for the ARO of 1,2-epoxyhexane on the impregnated catalyst. Furthermore, a significant increase in product selectivity was observed (EE of 87% vs 66% and 75% vs 65% for the ARO of 1,2-epoxyhexane and cyclohexene oxide, respectively). This can be attributed to the type of immobilisation; the impregnated catalyst is adsorbed onto the silica surface, which limits its activity, whereas the catalyst in the supported ionic liquid phase is more accessible for reaction. The leaching rate for the SILP is comparable to the leaching observed for the impregnated catalyst (3.1% over four runs).

After repeated recycling, the silica support material deteriorates due to the abrasive forces in the stirred reactor. As a result, the quantitative recovery of the silica material becomes more and more difficult. Because the chiral transition metal complex and the ionic liquid are expensive, their possible recovery after several batch reactions was examined. It was demonstrated that the dimeric Cr(salen) catalyst and the ionic liquid can be recovered almost quantitatively by Soxhlet extraction with acetone.

Table 2
Continuous flow experiment: ARO of 1,2-epoxyhexane



Run[a]	Eq. $TMSN_3$	Flow rate (ml/h)	Conversion (%)	EE epoxide (%)	EE product (%)	TON[b]	Leaching (%)
1	0.6	2.5	28	32	94	109	0.44
2	0.6	1.0	52	87	89	217	0.17
3	0.7	0.5	51	94	82	314	0.08

[a] Runs 1–3 are consecutive experiments with the same catalyst in a continuous flow reactor.

[b] The turn over number (TON) is the number of substrate molecules converted to product per catalyst molecule. The value is the cumulative TON over the 3 runs.

The issue of support deterioration can be avoided by using the catalyst in a continuous-flow reactor. Furthermore, it allows better control of the resolution reaction—more specifically, it is more suitable for fine-tuning the reaction in terms of recovery of the highly enantioenriched ring-opened product. By adjusting the flow rate and the amount of $TMSN_3$, the reaction can be tuned for epoxide or product selectivity (Table 2). Using a flow rate of 2.5 ml/h, the continuous-flow experiment offered a product enantioselectivity of 94% for the ARO of 1,2-epoxyhexane. This matches the reported EE of 97% for the homogeneous reaction with the monomeric Cr(salen) complex optimised for product selectivity. On the other hand, the reaction can also be adjusted to yield highly enantioenriched epoxide; with a flow rate of 0.5 ml/h and 0.7 Eq. of $TMSN_3$, 1,2-epoxyhexane was obtained with 94% EE. After three consecutive runs, a cumulative TON of 314 and an overall leaching of 0.7% were observed. This demonstrates the selectivity and the stability of this heterogeneous Cr(salen) catalyst over time.

4. Conclusion

A dimeric Cr(salen) catalyst was successfully immobilised in a supported ionic liquid and was shown to offer better reactivity and selectivity than the Cr(salen) complex immobilised by impregnation. It was also demonstrated that catalyst and ionic liquid can be recovered by Soxhlet extraction with acetone. Alternatively, a continuous-flow experiment showed the catalyst's excellent selectivity and stability over time and demonstrated that it can serve as an alternative for the homogeneous reaction.

Acknowledgments

This work was done under an IAP Program sponsored by the Belgian Federal Ministry of Science Policy. B.M.L.D. acknowledges a grant from K.U. Leuven.

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