Letter

Olefin epoxidation catalysed by Schiff-base complexes of Mn and Ni in heterogenised-homogeneous systems

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Abstract

M(salen) complexes (M = Mn(III), Ni(II); salen = bis-(salicyldene)ethylenediamine) have been encapsulated in zeolite Y and characterised. Mn(salen)$^+$ complex was also anchored in montmorillonite clay and characterised. Epoxidation of olefins, viz. cyclohexene, cyclooctene and 1-hexene with terminal oxidants (NaOCl, KHSO$_5$) was carried out with the anchored catalyst complexes and found that the epoxidation of linear olefin (1-hexene) is selectively facile than cyclic olefins. Experimental results are compared with those reported for M(salen) complexes catalysed olefin epoxidation in homogeneous and heterogenised-homogeneous catalytic conditions. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Olefin epoxidation; Salen complexes of Mn and Ni; Heterogenised-homogeneous catalysis; Zeolite; Montomorillonite

1. Introduction

Development of non-porphyrinic transition metal complexes as catalysts for oxidation of organic substrates is a part of our current research interest [1–4]. Recent trends [5–11] in immobilisation of catalyst complexes on insoluble solid support (mainly clay-based materials) appears to be a good way of heterogenising homogeneous catalysis. Such type of heterogenised-homogeneous catalytic systems not only offer the combined advantages of homogeneous (mild conditions) and heterogeneous (easy separation), but also impose extreme shape selectivity in catalytic process. This prompted us to initiate a research programme on oxo-transfer reaction catalysed by Schiff base/macrocyclic complexes of transition metals in heterogenised-homogeneous conditions. To begin with, M(salen) complexes (M = Mn(III), Ni(II); salen = bis-(salicyldene)ethylenediamine) were chosen which can effectively catalyse olefin epoxidation [12–14] in homogeneous conditions. In this paper we wish to report epoxidation of cyclohexene, cyclooctene and 1-hexene catalysed by M(salen) complexes anchored in zeolite and montmorillonite clay. Although Mn(III)-(salen)$^+$ complex had already been subjected to olefin epoxidation in heterogenised-homogeneous [6,15] conditions, most of these studies are limited to the use of iodosylbenzene (PhIO) as terminal oxidant. The present paper explores the possibility of using inexpensive and easy-to-handle oxidants like NaOCl, KHSO$_5$ in het-

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erogenised-homogeneous conditions which has not been studied so far (albeit one report exists [14] on the use of NaOCl as terminal oxidant in Ni(salen) catalysed olefin epoxidation in homogeneous conditions). Further, the present study would provide a rational approach toward development of such an important class of catalytic systems.

2. Experimental

There are two techniques for the preparation of zeolite encapsulated complexes which include a template synthesis or a flexible ligand such as salen, which can diffuse into the zeolite cage by twisting its way through the pores where, upon complexation with pre-exchanged metal, the ion becomes too large to exit. Preparation and encapsulation of Ni(salen) [2] and Mn(salen)$^+$ [6] in zeolite Y were achieved by following the procedure reported earlier [2,6]. Zeolite-Y encapsulated M(salen) complexes are designated as M(salen)Y in the text. Preparation of clay-supported Mn(salen)$^+$ complex involved stirring of 5 g of Na-montmorillonite (Fluka) with Mn(salen)$^+$ complex (2 g) in 100 ml of acetonitrile–water (50:50) mixture for 24 h. The clay-supported Mn(salen)$^+$ complex (Mn-(salen)–clay) was then filtered and washed with acetonitrile several times (until the absorption of the washings showed the absence of Mn(salen)$^+$). The UV–VIS spectrum of the solid product was found to be almost identical to the spectrum of Mn(salen)$^+$ in solution. Elemental analysis of solid Ni(salen)Y catalyst sample showed that it contained 3.5% (w/w) of Nickel. Mn content of Mn(salen)$^+$Y and Mn(salen)$^+$–clay were found to be 1.7% and 3.8%, respectively. All other chemicals were of A.R. grade and used as received. Catalytic oxidation reactions were performed at normal temperature and pressure. In a typically catalytic run 200 mg of supported catalyst complex, 0.15 mmol of CTAB (cetyl trimethyl ammonium bromide—a phase transfer catalyst), 10 mmol

of KHSO$_5$ (dissolved in 10 ml of water and pH of the solution adjusted at 7 with NaOH) or 15 ml of NaOCl (1 M) and 100 mmol of substrate was stirred in CH$_2$Cl$_2$ (25 ml) for 5 h and aliquots of CH$_2$Cl$_2$ were subjected to GC (Shimadzu GC-9A) analysis. No products were detected in the aqueous layer. GC parameters were quantified with the authentic samples of the reaction products.

3. Results and discussion

Catalytic oxidation of organic substrates (cyclohexene, cyclooctene and 1-hexene) were carried out with supported M(salen) complexes with NaOCl and KHSO$_5$ as terminal oxidants (see Section 2 for reaction conditions). A series of blank experiments revealed that each component is essential for an effective catalytic reaction and the system is relatively unaffected by changing the order of mixing. GC analysis of aliquots of CH$_2$Cl$_2$ layer showed the formation of substrate epoxides as major products with trace amount of alcohols (Table 1). Experimental results (Table 1) suggest the fact that M(salen) complexes in conjunction of NaOCl or KHSO$_5$ can effect the catalytic epoxidation of olefins in heterogenised conditions. All the anchored M(salen) complexes appeared to be stable under experimental conditions (as the catalysts recovered by filtration of the reaction mixture and washing with CH$_2$Cl$_2$ were found to be reactive for further catalytic runs), but undergo some degradation over 24 h as evidenced by some 10–15% loss of metal content. The selectivity of the heterogenised catalytic system was examined in a competitive epoxidation of 1-hexene and cyclohexene mixture (1:1). The results of the competitive epoxidation summarized in Table 2 indicate the preferential epoxidation of linear olefin (1-hexene). This is suggestive of the fact that the linear olefin under investigation (1-hexene) is sterically more approachable to the active sites and prevent the cyclic olefin (cyclohexene) accessing the active

Table 1
Epoxidation of olefins with supported M(salen) complexes[a]

Catalyst	Oxidant	Substrate	Product	Yield (%)[b]
Ni(salen)Y	NaOCl	Cyclohexene	Cyclohexene epoxide	13
			Cyclohexeneol	trace
		Cyclooctene	Cyclooctene epoxide	10
			Cycloocteneol	trace
		1-Hexene	1-Hexene epoxide	17
			Cycloocteneol	trace
		1-Hexene	1-Hexene epoxide	17
Ni(salen)Y	KHSO$_5$	Cyclohexene	Cyclohexene epoxide	11
			Cyclohexeneol	trace
		Cyclooctene	Cyclooctene epoxide	8.5
			Cycloocteneol	trace
		1-Hexene	1-Hexene epoxide	14
Mn(salen)$^+$Y	NaOCl	Cyclohexene	Cyclohexene epoxide	9
			Cyclohexeneol	2
		Cyclooctene	Cyclooctene epoxide	7.4
			Cycloocteneol	1.4
		1-Hexene	1-Hexene epoxide	11
Mn(salen)$^+$Y	KHSO$_5$	Cyclohexene	Cyclohexene epoxide	8
			Cyclohexeneol	trace
		Cyclooctene	Cyclooctene epoxide	6.8
			Cycloocteneol	trace
		1-Hexene	1-Hexene epoxide	
Mn(salen)$^+$–clay	KHSO$_5$	Cyclohexene	Cyclohexene epoxide	9.2
			Cyclohexeneol	trace
		Cyclooctene	Cyclooctene epoxide	7.6
			Cycloocteneol	trace
		1-Hexene	1-Hexene epoxide	12

[a] See Section 2 for reaction conditions.
[b] Based on substrate taken.

sites at an efficient rate. The kind of mechanism operative for the epoxidations of listed olefins in the zeolite pores or clay interlayers occupied by M(salen) catalyst complexes is very difficult to assign unambiguously. However, comparing the above experimental observations with those reported for M(salen) complexes catalysed olefin epoxidation in homogeneous solution [12,13], we propose a working mechanism (Eqs. (1) and (2)) for the epoxidation of the above olefins.

$$[M^n(salen)] + OX^- \rightarrow [M^{n+2}(salen)(O)] + X^-$$
(1)

$$[M^{n+2}(salen)(O)] + S \rightarrow [M^n(salen)] + SO$$
(2)
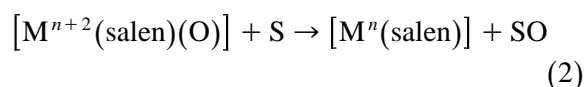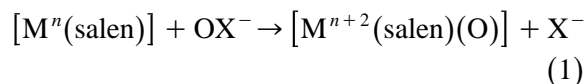
where M = Mn(III), Ni(II); OX$^-$ = OCl$^-$, HSO$_5^-$; X$^-$ = Cl$^-$, HSO$_4^-$; S = substrate (olefins); SO = substrate epoxide; $n = 3$ for M = Mn(III) and $n = 2$ for M = Ni(II).

We presume that the reaction proceeds through the formation of a high-valent oxo–metal complex as a catalytic intermediate (Eq. (1)), which subsequently transfer oxo-atom to the substrate to yield epoxide (Eq. (2)) as oxidation product. The change in the colour of M(salen) catalyst complexes (grayish-brown for Ni(salen) and darkening of the brown colour for Mn(salen) complexes) upon addition of KHSO$_5$ (or NaOCl) to the reacting systems probably implies the formation of high-valent metal–oxo species. Addition of strong two electron reductant like L-ascorbic acid immediately restored the original colour of the M(salen) complexes, which supports the arguments in favour of the formation of high-valent intermediate species

Table 2
Epoxidation of 1:1 (v/v) mixture of cyclohexene and 1-hexene catalysed by supported M(salen) complexes[a]

Catalyst	Oxidant	Substrate	Epoxide formation (%)[b]	
Ni(salen)Y	KHSO$_5$	Cyclohexene + 1-hexene	1-Hexene epoxide (6)	Cyclohexene epoxide (3)
Ni(salen)Y	NaOCl	Cyclohexene + 1-hexene	1-Hexene epoxide (7)	Cyclohexene epoxide (2)
Mn(salen)$^+$Y	NaOCl	Cyclohexene + 1-hexene	1-Hexene epoxide (6)	Cyclohexene epoxide (2)
Mn(salen)$^+$–clay	KHSO$_5$	Cyclohexene + 1-hexene	1-Hexene epoxide (5)	Cyclohexene epoxide (2)

[a] See Section 2 for reaction conditions.
[b] Based on substrate taken.

during the course of the reaction. A comparison of the effectiveness of olefin epoxidation with M(salen) complexes in homogeneous and heterogenised-homogeneous conditions is shown in Table 3. The lower rate of epoxidation with supported catalysts is presumably associated with the diffusion of substrates and oxidant towards the active sites (i.e., where the metal complex is situated inside the insoluble support) and channel of products out (i.e., counter diffusion). The formation of high-valent metal–oxo species in the reaction between catalyst complex and terminal oxidant (Eq. (1)) is an important part of the catalytic cycle. We had reported

earlier [16] that the formation of high-valent metal–oxo species is a two-electron and one-atom transfer process and it takes place through an innersphere manner (and hence substitution controlled). Hence, the nucleophilicity of the terminal oxidants (along with the oxidation potentials) plays an important role towards the formation of metal–oxo intermediates. However, the results of olefin epoxidation (Table 3) with immobilized M(salen) complexes are not changed greatly by changing the terminal oxidants. The accumulated data in Table 3 suggest that the incorporation of oxidant oxygen atom to the substrate occurs through the transfer of oxy-

Table 3
Epoxidation of olefins catalysed by M(salen) complexes in homogeneous and heterogenised-homogeneous conditions

Catalyst	Oxidant	Substrate	Product	Yield (%)[a]	Ref.
Ni(salen)[b]	NaOCl	Cyclohexene	Cyclohexene epoxide	23	[14]
Ni(salen)Y[c]	NaOCl	Cyclohexene	Cyclohexene epoxide	13	this work
Ni(salen)Y[c]	KHSO$_5$	Cyclohexene	Cyclohexene epoxide	11	this work
Mn(salen)$^{+}$ [d]	PhIO	Cyclohexene	Cyclohexene epoxide	15	[15]
Mn(salen)$^+$Y[e]	PhIO	Cyclohexene	Cyclohexene epoxide	14	[6]
Mn(salen)$^+$Y[c]	NaOCl	Cyclohexene	Cyclohexene epoxide	9	this work
Mn(salen)$^+$Y[c]	KHSO$_5$	Cyclohexene	Cyclohexene epoxide	8	this work
Mn(salen)$^+$–clay (kaolinite)[f]	PhIO	Cyclohexene	Cyclohexene epoxide	7.5	[15]
Mn(salen)$^+$–clay (kaolinite)[g]	t-BuOOH	Cyclohexene	Cyclohexene epoxide	8.6	[15]
Mn(salen)$^+$–clay (montmorillonite)[c]	KHSO$_5$	Cyclohexene	Cyclohexene epoxide	9.2	this work

[a] Based on substrate taken.
[b] Ni(salen) catalyst (0.1 mmol), benzyltributylammoniumbromide (0.15 mmol), cyclohexene (4.0 mmol) in CH$_2$Cl$_2$ (10 ml) were stirred with 20 ml NaOCl (0.77 M) for 5 h.
[c] See Section 2 for reaction conditions.
[d] Mn(salen)$^+$ (0.002 mmol), PhIO (0.068 mmol) and cyclohexene (0.2 mmol) in CH$_3$CN (2 ml) were stirred for 45 min.
[e] 100 mg of zeolite encapsulated catalyst, 25 mg of PhIO and cyclohexene (0.2 mmol) in CH$_3$CN (5 ml) were stirred for 16 h.
[f] 150 mg of clay supported catalyst, 15 mg of PhIO and cyclohexene (0.2 mmol) in CH$_3$CN (2 ml) were stirred for 45 min.
[g] 800 mg of clay-supported catalyst, t-BuOOH (0.4 mmol), cyclohexene (0.6 mmol) imidazole (0.132 mmol) in CH$_3$CN (5 ml) were stirred for 3 h.

gen atom from high-valent metal–oxo intermediate to the olefinic double bond. This step is perhaps rate-limiting, but diffusion controlled. The results of epoxidation with smectite-clay-supported $Mn(salen)^+$ further support our arguments as the swollen interlayers of montmorillonite permit comparatively rapid diffusion. However, a high conversion of olefins to epoxides catalysed by $Mn(salen)^+$ immobilised in rigid macroporous polymeric network (which barely swells ($< 5\%$) in common solvents) reported recently [17], may be attributed to the predominant localization of the catalytic sites in the accessible region of the polymer matrices.

4. Conclusion

Above preliminary results show that Schiff-base complexes of Mn and Ni immobilized in the pores of zeolite or interlaminar space of montmorillonite can act as operable epoxidation catalysts either in presence of $KHSO_5$ (or NaOCl). Selectivity in epoxidation of linear olefins is to be the result of small pore size of the zeolite host which governs the molecular sieving and orientation properties. However, the system suffers from some problems namely low rate of formation of products and low turnovers which are presumably associated with the diffusion of substrates and oxidant towards the active sites (i.e., where the metal complex is situated inside the solid support) and channel of product out (i.e., counter diffusion). Nevertheless, active research pertinent to the above matter is in progress in order to promote the potential use of such anchored catalysts in selective catalytic reactions.

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