Asymmetric epoxidation of stilbene by manganese(III) chiral salen complex immobilized in Al-MCM-41

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Manganese-exchanged MCM-41 modified with a chiral salen is an effective enantioselective heterogeneous epoxidation catalyst for *cis*-stilbene.

Interest in asymmetric synthesis continues to increase and this has highlighted the need for the design of highly selective asymmetric catalysts. Most of this research activity concerns homogeneous catalysts, but there is now increased interest in the identification of suitable heterogeneous asymmetric catalysts, since such catalysts readily overcome the problems typically encountered with homogeneous systems, namely product recovery and catalyst separation. To date, three approaches have been taken in the design of heterogeneous enantioselective catalysts: (*i*) the use of a chiral support for an achiral metal catalyst,[1] (*ii*) modification of an achiral heterogeneous catalyst using a chiral cofactor,[2–4] and (*iii*) the immobilisation of a homogeneous catalyst.[5] Most attention and success has been observed with enantioselective hydrogenation catalysts.[2–6]

One of the biggest challenges remaining for catalytic chemists is the design of heterogeneous enantioselective oxidation catalysts; this is a topic that retains intense research interest, but, to date, is significantly less advanced than the research into enantioselective hydrogenation catalysts. Interest in heterogeneous oxidation catalysts was stimulated by the discovery that the microporous titanium silicalite TS-1 is an effective catalyst for epoxidation reactions at 25–60 °C using hydrogen peroxide as oxidant, and this has led to the observation that a broad range of microporous and mesoporous materials are active oxidation catalysts.[7] However, to date these titanium-containing systems have not been successfully modified to act as heterogeneous enantioselective catalysts. In contrast, there has been significant research interest in homogeneous enantioselective epoxidation catalysts and in this area there has been significant success.[8–11] In particular, chiral manganese salen complexes are very effective as asymmetric homogeneous epoxidation catalysts for *cis*-substituted aryl alkenes.[11–13] The identification of heterogeneous counterparts has been somewhat slower and for manganese complexes three approaches have been adopted: (*i*) supporting Mn–salen alkene epoxidation catalysts on polymers,[14–16] (*ii*) ion exchange of manganese complexes into the intra-crystalline space of zeolites, *e.g.* zeolite Y[17] or mesoporous materials,[18] and (*iii*) encapsulation of manganese complexes within zeolites by synthesis using 'ship-in-a-bottle' methodology.[19] Considerable progress has been made using polymer-supported systems,[14] but the use of inorganic supports has received far less attention. Preformed manganese complexes have been

ion-exchanged in zeolites but only using manganese complexes with achiral nitrogen ligands, *e.g.* bipyridyl.[20] Ogunwumi and Bein[19] have demonstrated that the 'ship-in-a-bottle' approach can be successfully used to synthesize the asymmetric manganese salen complex inside the cages of the zeolite EMT. The molecular cross section of the manganese salen complex is too large for the ion-exchange method to be employed successfully. Although this approach does produce an asymmetric epoxidation catalyst, the pore size of the zeolite can limit the effective range of substrates that can be utilized. Here we demonstrate the synthesis of a heterogeneous enantioselective epoxidation catalyst for the larger substrate *cis*-stilbene by combining manganese(III) salen with the mesoporous Al-MCM-41 (Scheme 1). This work extends the methodology previously identified in our studies concerning the enantioselective aziridination of alkenes using Cu²⁺-exchanged zeolite Y modified with bis(oxazolines).[21]

Al-MCM-41 was synthesized according to literature methods[22] and ion exchanged with aqueous Mn(OAc)₂ (0.2 M, 25 °C, 24 h), filtered, washed with water and vacuum dried. This procedure was repeated twice and the resulting material was calcined (550 °C, 24 h) (Mn content 2.0% by weight). The calcined Mn-exchanged Al-MCM-41 was heated under reflux with the chiral salen ligand, (*R,R*)-(−)-*N,N*'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (Aldrich), in CH₂Cl₂ (24 h, Mn : salen = 1 : 1), cooled to 0 °C and washed with CH₂Cl₂. This procedure resulted in incorporation of 10% of the chiral salen ligand (determined by TGA and solution analysis). The Mn-exchanged Al-MCM-41 : salen catalyst (2.0 Mn% by weight, Mn : salen = 1 : 0.1 mol ratio) was investigated for the epoxidation of *cis*-stilbene using iodosylbenzene as oxidant; the results, together with those of control
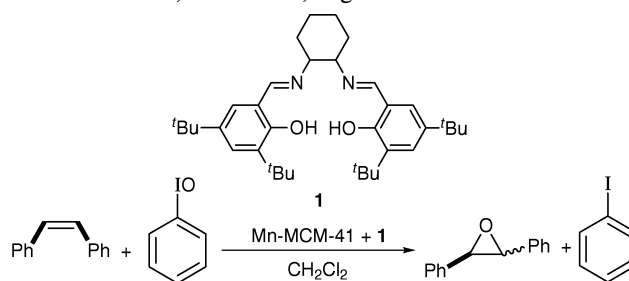
Scheme 1

Table 1 Epoxidation of stilbene at 25 °C using Mn-exchanged MCM-41

Entry	Catalyst	Time[a]/h	Conversion[b,c]	Epoxide yield[c] (%)	Selectivity[c] (%)		e.e. trans[d] (%)
					cis	trans	
1	None	25	0	0	0	0	0
2	Mn(OAc)$_2$[e,f]	24	100	1.5	0	100	0
3	Mn–salen complex[e]	1	100	86	29	71	78
4	Al-MCM-41[e]	24	0	0	—	—	—
5	Mn-MCM-41[e]	2	45	3	0	100	0
6	Mn-MCM-41 + salen[e]	2	100	69	58	42	70
7	Mn-MCM-41 + salen[e,g]	26	100	35	0	100	25
8	Solution[e]	2	0	0	—	—	—
9	Mn-MCN-41 reused[e]	2	37	18	61	39	30
10	Mn-MCM-41 recalcined + salen[e]	2	100	52	63	37	54

[a] Reaction time. [b] As determined by decomposition of iodosylbenzene to iodobenzene, using HPLC. [c] Conversions, yields and selectivity determined by HPLC, using APEX ODS reverse-phase column. [d] Enantiomeric excess determined by chiral HPLC using (R,R) Whelk-O 1 column, 92% hexanen–Pr^{i}OH. [e] Reactions were conducted in CH$_2$Cl$_2$ unless otherwise noted with molar ratio of cis-stilbene : catalyst : iodosylbenzene = 7 : 1 : 0.13. [f] Reaction conducted in CH$_3$OH. [g] trans-Stilbene used as substrate.

experiments, are shown in Table 1. Mn(OAc)$_2$, in the absence of MCM-41 or salen ligand, is not a particularly active catalyst; only 1.5% yield of the epoxide is formed after reaction for 24 h at 25 °C and only the trans-epoxide is formed (entry 2). Modification of manganese in solution by the chiral salen ligand as expected leads to a significant rate enhancement, but the cis-epoxide is also formed (entry 3) and the trans-epoxide is formed with 78% e.e. Interestingly, immobilization of the manganese by Al-MCM-41 (entry 5) leads to an increase in reactivity when compared with the non-manganese-exchanged parent material (Al-MCM-41, entry 4), whereas non-immobilised Mn^{3+} in the absence of the salen ligand is inactive (entry 2). This effect suggests that the Al-MCM-41 is occupying part of the manganese coordination sphere and that this restricts the cis to trans transformation. Modification of the Mn-exchanged Al-MCM-41 with the salen ligand leads to a further enhancement in reactivity and the cis : trans ratio of the epoxide. The trans epoxide is formed with an e.e. of 70% (entry 6), which is very similar to that observed for the equivalent homogeneous reactions (entry 3). The turnover rates, based on the amount of Mn–salen, for the heterogeneous catalyst were found to be higher than those for the homogeneously catalysed reaction, this is in contrast to previous studies when comparable turnover rates have been observed. In the present study the turnover rates [mol epoxide (mol Mn–salen)$^{-1}$/h^{-1}] are found to be 26 for the heterogeneous reaction and 7 for the homogeneous reaction. trans-Stilbene (entry 7) was found to be a significantly less reactive substrate and the e.e. of the resulting trans-epoxide was significantly decreased. The use of Mn-exchanged Al-MCM-41 : salen catalyst for this epoxidation does not result in the formation of significant levels of by-products as has been observed when manganese bypyridyls have been used as catalysts,[19] and typically only deoxybenzoin is observed at low levels (ca. 5–10%, based on iodosylbenzene) although some decomposition of iodosylbenzene is observed (ca. 30%).

A further set of experiments was carried out to examine the reusability of the Mn-exchanged Al-MCM-41 : salen catalyst. Following the reaction, the Mn-exchanged Al-MCM-41 : salen catalyst was recovered by filtration and the solid reused in a new catalytic reaction (entry 9); although the reactivity and enantioselectivity declined, epoxide was still formed, and the cis : trans ratio was practically unchanged. Recalcina-tion of the recovered material and addition of new salen ligand essentially restored the catalytic activity and the enantioselection (entry 10). Use of the solution following filtration did not give any reaction (entry 8), and furthermore this solution contained no Mn^{3+} although some salen leaching was observed. These experiments demonstrate that the reaction occurring with Mn-exchanged Al-MCM-41 : salen is wholly catalysed heterogeneously.

This study demonstrates that Mn-exchanged Al-MCM-41 when modified by a chiral salen ligand can be an effective enantioselective heterogeneous epoxidation catalyst, and these results extend the generality of the methodology described in our earlier studies of asymmetric enantioselective aziridination using Cu^{2+}-exchanged zeolites.[21]

Acknowledgements

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22 C. T. Kresge, M. E. Leonowisc, W. J. Roth, J. C. Vartulli and J. S. Beck, *Nature* (*London*), 1992, **359**, 710. $C_{12}H_{25}(CH_3)_3NOH/Cl$ solution (61.3 g) was stirred with water (160 g) and then sodium aluminate (2.77 g) was added slowly. Silica (16.7 g, fumed), tetramethylammonium silicate solution (46.7 g, 25 wt.%) and tetramethylammonium hydroxide solution (8.8 g, 25 wt.%) were added with stirring. The mixture was reacted in an autoclave (100 °C, 24 h) after which time the solid material was collected, washed with water and calcined (550 °C; N_2, 4 h; air, 12 h). BET: N_2 adsorption–desorption measurements at -178 °C confirmed that this material was mesoporous. Average pore diameter: 38 Å. The powder X-ray diffraction pattern of the solid sample gave results in agreement with spectra published in the literature.