

Highly effective catalysts of natural polymer supported Salophen Mn(III) complexes for aerobic oxidation of cyclohexene

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Received 9 May 2005; received in revised form 29 November 2005; accepted 31 December 2005

Available online 7 February 2006

Abstract

Three chitosan (abbreviated as CS) supported Salophen Mn(III) complexes were prepared in a simple way and characterized by FT-IR and XPS. Their abilities to catalyze allylic oxidation of cyclohexene with oxygen in the absence of solvents or reducing agents were studied. It has been revealed that the amino groups of CS coordinated with the Mn atoms of Salophen Mn(III) complexes to form CS–Salophen Mn(III) complexes, which have much better catalytic activities for allylic oxidation of cyclohexene than the corresponding unsupported Salophen Mn(III) complexes. Under reaction conditions of 343 K and ambient pressure of oxygen, after 12 h reaction, the cyclohexene oxidation catalyzed by CS–Salophen Mn(III) complex resulted in 11.03×10^4 turnover numbers (based on the manganese atom), which was about 44 times as large as that by unsupported Salophen Mn(III) complex. The influences of reaction temperature and reaction time on the oxidation of cyclohexene were also investigated.

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Keywords: Chitosan; Supported; Schiff base; Oxygen; Cyclohexene oxidation

1. Introduction

The allylic oxidation of olefin into α,β -unsaturated ketones is an important transformation in natural product synthesis [1]. In particular, the oxidation products of cyclohexene and their derivatives, viz. 2-cyclohexen-1-one, 1-methylcyclohex-1-en-3-one, etc., are important in organic synthesis owing to the presence of a highly reactive carbonyl group, which is utilized in cycloaddition reactions [2–4]. Great efforts have been devoted to the oxidation of cyclohexene in the past years [5–13]. Direct conversion of cyclohexene into adipic acid with H_2O_2 catalyzed by $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ combined with PTC has been reported by Sato et al. [14]. However, most processes reported suffer from relatively harsh conditions or poor conversions and selectivities. Awareness of environmental issues has proven a potent driving force in the development of environmentally friendly processes and technologies in the chemical industry [15,16]. In this aspect, more efficient catalytic system for oxidation of cyclohexene with molecular

oxygen without any solvents or reducing agents is particularly desirable.

Manganese Schiff base complexes are known to be active homogeneous catalysts in the epoxidation of olefins with various stoichiometric oxidants [17] such as peroxides, NaOCl or PhIO. The chiral manganese Schiff base catalysts developed by Jacobsen and co-workers are active and enantioselective epoxidation catalysts known to date [18]. Due to the inherent advantages of heterogeneous catalysts over homogeneous catalysts, much effort [19–22] has been made to immobilize these homogeneous catalysts onto solid supports, such as polymers [23], clays [24] and zeolites [22,25]. However, catalysts based on biopolymers have not received much attention.

Chitosan, the most abundant natural amino polysaccharide, is produced by the deacetylation of chitin, which is one of the key constituents of the shells of crustaceans and is a by-product of the fishing industry. It is readily formed into films or fibres for many applications [26]. The flexibility of the material, insoluble in the vast majority of solvents, but capable of being cast into films and fibres from dilute acid, along with its inherent chirality makes chitosan an excellent candidate for a support of catalyst. In this respect, several catalytic systems using chitosan as supports have been developed [27–35]. Functionalization of

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the chitosan to provide co-ordination sites has also been carried out and has provided catalysts for oxidation reactions and Suzuki and Heck reactions [36–38]. We previously reported that Schiff base copper complexes derived from chitosan and substituted salicylaldehydes were efficient catalysts for the cyclopropanation of styrene [39,40]. In this paper, we prepared chitosan supported Schiff base Mn(III) complexes and investigated their catalytic abilities in the oxidation of cyclohexene with oxygen without any solvents or reducing agents. High turnover numbers and selectivities were obtained.

2. Experimental

2.1. Materials and equipments

2,4-di-*tert*-Butylphenol was purchased from Fluka. Chitosan finely purified to a de-acetyl degree of 90.0% and with viscosity molecular weight (Mv) of 9.6×10^5 was provided by researcher Ai-Qin Wang (Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences). Salicylaldehyde, cyclohexene and *o*-phenylenediamine were repurified before use. Other reagents were of analytical grade and were used as received. 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and 5-nitro-2-hydroxybenzaldehyde were synthesized according to the procedure described in the literatures [41,42]. Salophen Mn(III) complexes **2a–c** were prepared as described in the literature [43] (Scheme 1). FT-IR spectra were measured on a Nexus 870 FT-IR spectrophotometer. XPS measurements were performed with a VG Scientific ESCALAB 210 instrument with Mg K α radiation (1253.6 eV). Atomic absorption results were obtained on a Hitachi 180-80 polarized Zeeman atomic absorption spectrophotometer. The reaction products of oxidation were determined by an HP 6890/5973 GC/MS instrument and analyzed by an Agilent 6820 gas chromatograph.

2.2. Preparation of chitosan supported Salophen Mn(III) complexes

Chitosan (2.0 g, equivalent to 10.80 mmol NH₂) was dissolved in 150 mL dilute acetic acid at 50 °C and stirred vig-

Table 1
The IR date of CS and CS–Salophen Mn(III) complexes

Selective IR bands (cm ⁻¹)	Substances			
	CS	CS– 2a	CS– 2b	CS– 2c
$\nu_{\text{N-H}}$	3473	3422	3427	3422
$\delta_{\text{N-H}}$	1601	–	–	–

orously till the solution became clear. The pH of the solution was adjusted to 7 by addition of an aqueous solution of Na₂CO₃ (1%), and then, a second solution containing 0.15 mmol Salophen Mn(III) complex (**2a–c**) in 50 mL ethanol was added dropwise to the first solution. After stirred continuously for 20 h in these conditions, the mixture was separated by filtration. The solid was copiously washed with ethanol and acetone, dried at 90 °C under vacuum for 12 h to give chitosan supported Salophen Mn(III) (CS–**2a–c**) catalysts, which were then used for the oxidation of cyclohexene with molecular oxygen in the absence of solvents or reducing agents.

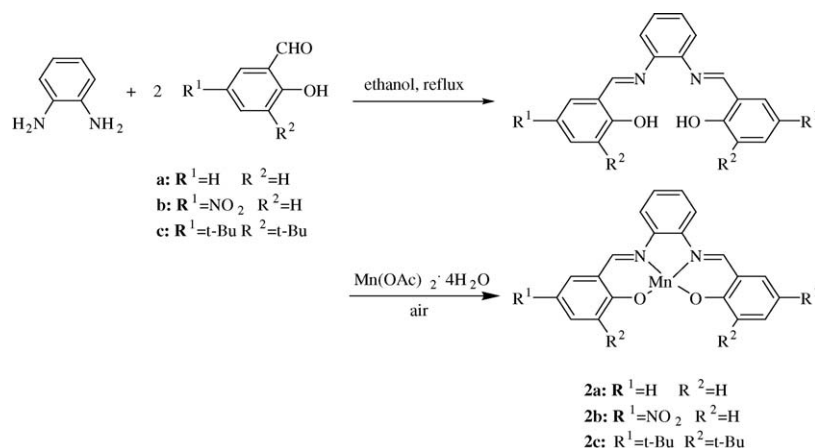
The metal contents of CS–**2a–c** determined by atomic absorption spectroscopy are 0.31, 0.59, and 0.56%, respectively.

2.3. Characterization of the catalysts

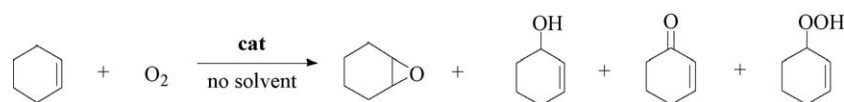
The catalysts obtained were characterized by FT-IR and XPS. The FT-IR spectrum of CS has a strong and broad absorption at 3473 cm⁻¹ which masks the N–H stretching band. However, in CS–**2a–c**, this absorption shifted to 3422, 3427, and 3422 cm⁻¹ respectively (Table 1). The absorption at 1601 cm⁻¹ on CS can be attributed to bending vibration of NH₂, but in CS–**2a–c** this absorption disappeared.

The data of XPS are shown in Table 2. It can be seen that after supporting, the binding energies of N 1s_{1/2} (in NH₂) increased and the binding energies of Mn 2p_{1/2} and Mn 2p_{2/3} decreased as expected (Table 2).

From the data of FT-IR and XPS, it can be concluded that the amino groups of chitosan coordinated with the manganese atoms of Salophen Mn(III) complexes to form CS–Salophen Mn(III) complexes.



Scheme 1. Procedure for synthesis of salophen Mn(III) complexes.



Scheme 2. Oxidation of cyclohexene.

Table 2
The data of X-ray photoelectron spectroscopy (XPS)

XPS peak	Binding energy (eV)						
	CS	2a	2b	2c	CS-2a	CS-2b	CS-2c
N 1s _{1/2} (NH ₂)	398.1	–	–	–	399.8	399.8	399.9
Mn 2p _{1/2}	–	654.4	654.4	654.2	652.8	652.2	651.7
Mn 2p _{3/2}	–	642.7	642.0	642.6	640.7	640.1	640.9

2.4. Oxidation of cyclohexene

Typical oxidation of cyclohexene was performed according to the procedure described in the literature [21]: a glass flask was charged with catalyst (2.0 mg) and cyclohexene (2.0 mL). The dry oxygen was filled from the gauge glass and the atmosphere was discharged out of the glass reactor with the gas outlet tube. The gas outlet tube was closed. The reactor was put into a bath, which had been heated to the desired temperature, and stirring was started. The consumption of oxygen was measured by the gauge glass. After the reaction, the samples were identified by GC-MS and quantified by GC. The products of the reaction were cyclohexene oxide (I), 2-cyclohexene-1-ol (II), 2-cyclohexene-1-one (III) and 2-cyclohexene-1-hydroperoxide (IV) (Scheme 2):

3. Results and discussion

3.1. Catalysis of Salophen Mn(III) and CS–Salophen Mn(III) complexes for oxidation of cyclohexene

The results of cyclohexene oxidation catalyzed by Salophen Mn(III) and CS–Salophen Mn(III) complexes are listed in Table 3. As can be seen, CS–Salophen Mn(III) complexes had great catalytic activities for oxidation of cyclohexene and high turnover numbers have been obtained. The conversion of cyclo-

hexene was higher for CS–2c than for CS–2a and CS–2b but the highest value of turnover numbers were obtained in the presence of CS–2a. The distribution of oxidation products was also different for the different catalysts. In the same conditions, the selectivity of 2-cyclohexene-1-one in the presence of CS–2a was the highest.

Compared with corresponding unsupported Salophen Mn(III) complexes, CS–Salophen Mn(III) complexes had much greater catalytic activities for aerobic oxidation of cyclohexene and much higher turnover numbers have been obtained (Table 3). A possible explanation for increase in catalytic activities due to supporting is that the active sites isolating effect of macromolecular supports made Salophen Mn(III) complexes disperse molecularly on chitosan while the neat complexes are not dispersed molecularly in the reaction mixture.

In order to investigate the catalytic activity of the CS–Salophen Mn(III) complexes, a series of experiments were carried out by choosing CS–2a as catalyst to investigate the influence of reaction temperature and reaction time.

3.2. The effect of reaction temperature

The catalytic activity of CS–2a depended on temperature. As shown in Fig. 1, the rise in reaction temperature increased the conversion of cyclohexene and great enhancement of the conversion occurred when reaction temperature increased from 60 to 70 °C. As for the distribution of the products, with increasing reaction temperature, the selectivities of 2-cyclohexene-1-one increased but the selectivity of cyclohexene oxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-hydroperoxide decreased, and the crucial changes occurred when reaction temperature increased from 60 to 70 °C.

Fig. 2 shows the effect of temperature on oxygen consumption with reaction time prolonged. It is clear that high reaction temperature raised the oxygen consumption. The average

Table 3
Comparison of catalytic activities of CS–Salophen Mn(III) complexes with unsupported Salophen Mn(III) complexes

Catalysts	Metal content (%)	Conversion ^a (%)	TON ^b (×10 ⁴)	Selectivities ^a (%)			
				I	II	III	IV
CS–2a	0.31	75.5	11.03	6.7	18.0	56.5	18.8
CS–2b	0.59	67.0	5.14	10.7	18.6	36.9	33.8
CS–2c	0.56	79.1	6.37	12.1	15.8	38.8	33.3
2a ^c	14.89	83.6	0.25	5.2	23.5	61.3	10.0
2b ^d	11.97	73.7	0.28	7.8	27.3	57.6	7.3
2c ^c	9.26	82.3	0.40	6.1	25.4	59.3	9.2

Conditions: catalyst 2.4 mg, cyclohexene 2.0 mL (19.7 mmol), 70 °C, 12 h.

^a Conversion and selectivity were determined by GC.

^b Moles of substrate converted per mole of metal in the catalyst.

^c Reaction in 5 mL CH₂Cl₂.

^d Reaction in 5 mL CH₃CN.

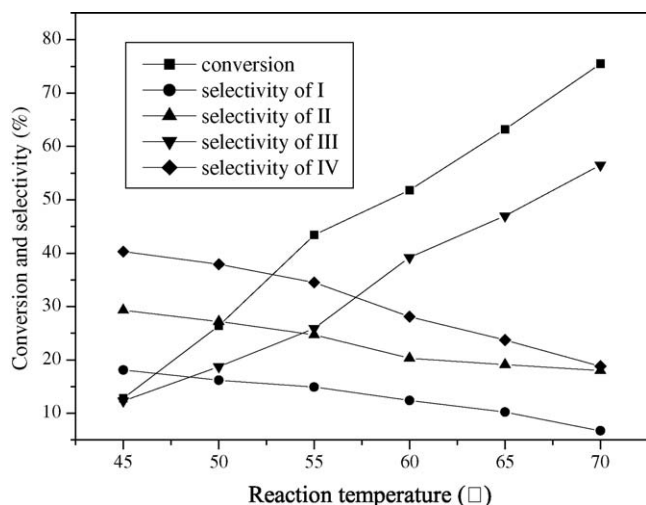


Fig. 1. The effect of reaction temperature on cyclohexene conversion and selectivities of the products. Conditions: catalyst 2.4 mg, cyclohexene 2.0 mL (19.7 mmol), 12 h.

oxygen consumption rate at 343 K is 1.4, 2.9 and 4.3 times as high as that at 333, 323, and 313 K, respectively. When the reaction temperature increased or the reaction time was prolonged, the cyclohexene conversion increased quickly but the selectivity of 2-cyclohexene-1-hydroperoxide decreased. It is indicative of a free radical reaction pathway [21].

3.3. The effect of reaction time

Fig. 3 shows how cyclohexene conversion and the selectivities of the products changed with reaction time. As the reaction time was prolonged, the cyclohexene conversion and the selectivity of 2-cyclohexene-1-one increased, while the selectivities of cyclohexene oxide and 2-cyclohexene-1-ol decreased. For 2-cyclohexene-1-hydroperoxide, the selectivity increased at first and then decreased. Fig. 3 shows that the increase of cyclohexene conversion dropped after 8 h reaction.

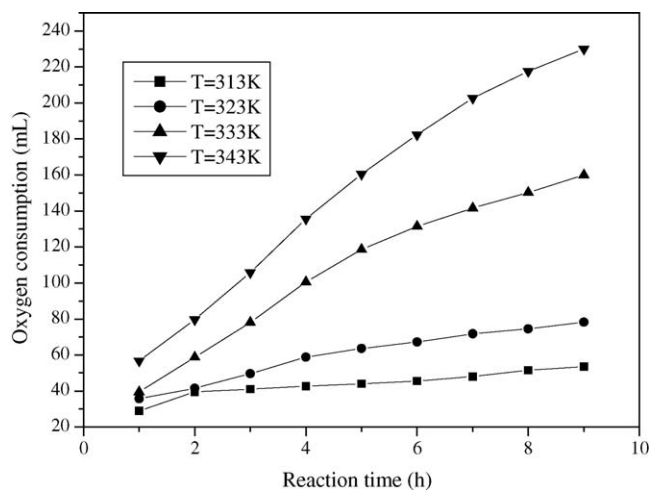


Fig. 2. The relationship between oxygen consumption and reaction time at different temperature. Conditions: catalyst 2.4 mg, cyclohexene 2.0 mL (19.7 mmol), 9 h.

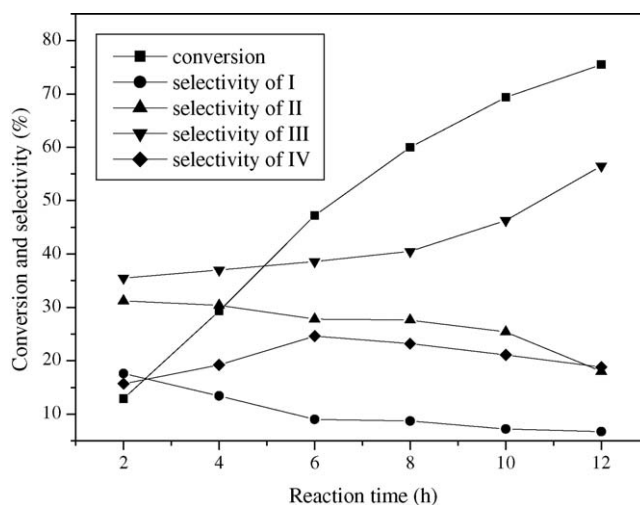


Fig. 3. The effect of reaction time on cyclohexene conversion and selectivities of the products. Conditions: catalyst 2.4 mg, cyclohexene 2.0 mL (19.7 mmol) 70 °C, 12 h.

3.4. Reuse of the catalysts

To investigate the reusability of CS-2a, the catalysts were separated by filtration after the first run, dried at 90 °C under vacuum and then used for the second run under the same conditions. The data obtained are listed in Table 4. As shown in Table 4, the selectivities of the products had no great changes after four times runs. The conversion of cyclohexene dropped sharply after the first run and then kept constant, which could be mainly attributed to the loss of loose Salophen Mn(III) complex on CS during the first run.

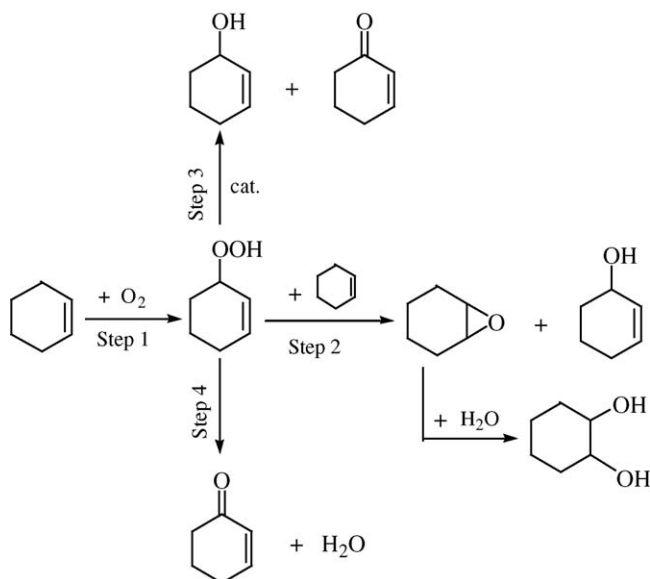
3.5. Discussion

According to the literature [9,44], the oxidation of cyclohexene with molecular oxygen initially forms 2-cyclohexene-1-hydroperoxide as shown in Scheme 3 (step 1). 2-Cyclohexene-1-hydroperoxide is not stable and can form cyclohexene oxide and 2-cyclohexene-1-ol by epoxidation of cyclohexene (step 2), decompose to 2-cyclohexene-1-ol and 2-cyclohexene-1-one in the presence of catalyst (step 3), or decompose to 2-cyclohexene-1-one and water (step 4). The conversion of cyclohexene is controlled by the rate of step 1 in Scheme 3 and the selectivity for cyclohexene oxide and 1,2-cyclohexandiol is controlled by the rate ratio of step 2 to steps 3 and 4.

Table 4
Reuse of the catalysts^a

Recycle no.	Conversion (%)	TON ($\times 10^4$)	Selectivities (%)			
			I	II	III	IV
Fresh	75.5	11.03	6.7	18.0	56.5	18.8
1	70.4	10.28	7.8	19.9	54.7	17.6
2	71.6	10.46	6.9	20.1	53.9	19.1
3	69.8	10.20	7.2	17.3	55.2	20.3
Average	71.8	10.49	7.2	18.8	55.1	19.0

^a Conditions: catalyst 2.4 mg, cyclohexene 2.0 mL (19.7 mmol), 70 °C, 12 h.



Scheme 3.

As shown in Figs. 1–3, with increasing reaction temperature or prolonged reaction time, the conversion of cyclohexene and the selectivity of 2-cyclohexene-1-one increased, which indicates that high temperature or long reaction time is of advantage to steps 1 and 4 in Scheme 3. Moreover, the selectivity of 2-cyclohexene-1-one in this study is much higher than that of 2-cyclohexene-1-ol, which indicates that the rate of step 4 was much faster than the rate of step 2. Once 2-cyclohexene-1-hydroperoxide formed, it converts to 2-cyclohexene-1-one and water very quickly. No 1,2-cyclohexanediol was detected, which indicates that cyclohexene oxide can hardly be hydrolyzed under these experiment conditions.

4. Conclusions

Chitosan supported Salophen Mn(III) complexes prove to be active and reusable catalysts for cyclohexene oxidation with oxygen in the absence of reducing agents or solvents; high cyclohexene conversion, turnover numbers and selectivity can be obtained. Chitosan is cheap and plentiful, and possesses particular microstructure, lower acidity (compared to supports such as silica) and excellent function; the catalysts are easy to prepare and can be easily separated after the reaction, which endow chitosan supported Salophen Mn(III) complexes with a bright future in industrial applications. This work, along with other published work, indicates that chitosan is a particularly interesting support for catalysts and its inherent chirality will form the basis for further applications of this fascinating material.

Acknowledgements

The authors are grateful to the National Natural Sciences Foundation of China (20373082, 29933050) for financial support.

References

- [1] G. Cainelli, G. Cardillo, Chromium Oxidation in Organic Chemistry, Springer-Verlag, Berlin, 1984.
- [2] K.B. Wiberg, Oxidation in Organic Chemistry, Academic Press, New York, 1965.
- [3] W.A. Waters, Mechanisms of Oxidation of Organic Compounds, Methuen, London, 1964.
- [4] A.B. Smith, J.P. Konopelski, J. Org. Chem. 49 (1984) 4094.
- [5] S.-H. Lau, V. Caps, K.-W. Yeung, K.-Y. Wong, S.C. Tsang, Micropor. Mesopor. Mater. 32 (1999) 279.
- [6] P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, J. Catal. 202 (2001) 245.
- [7] A. Sakthivel, S.E. Dapurkar, P. Selvam, Appl. Catal. A: Gen. 246 (2003) 283.
- [8] N. Sehlotho, T. Nyokong, J. Mol. Catal. A: Chem. 209 (2004) 51.
- [9] Y. Liu, K. Murata, M. Inaba, H. Nakajima, M. Koya, K. Tomokuni, Chem. Lett. 33 (2004) 200.
- [10] J.P.M. Niederer, W.F. Hölderich, Appl. Catal. A: Gen. 229 (2002) 51.
- [11] J. Połtowicz, E.M. Serwicka, E. Bastardo-Gonzalez, W. Jones, R. Mokaya, Appl. Catal. A: Gen. 218 (2001) 211.
- [12] Ewa M. Serwicka, J. Połtowicz, K. Bahranowski, Z. Olejniczak, W. Jones, Appl. Catal. A: Gen. 275 (2004) 9.
- [13] Dever M. Boghaei, S. Mohebi, Tetrahedron 58 (2002) 5357.
- [14] K. Sato, M. Aoki, R. Noyori, Science 281 (1998) 1646.
- [15] Dai E. Pei-Shing, Catal. Today. 26 (1995) 3.
- [16] R.A. Sheldon, J. Mol. Catal. A. 107 (1996) 75.
- [17] K. Srinivasan, P. Michaud, J.K. Kochi, J. Am. Chem. Soc. 108 (1986) 2309.
- [18] W. Zhang, J.L. Leobach, S.R. Wilson, E.N. Jacobsen, J. Am. Chem. Soc. 112 (1990) 2801.
- [19] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
- [20] H.-X. Feng, R.-M. Wang, Y.-F. He, Z.-Q. Lei, Y.-P. Wang, C.-G. Xia, J.-S. Suo, J. Mol. Catal. A: Chem. 159 (2000) 25.
- [21] R.-M. Wang, C.-J. Hao, Y.-P. Wang, S.-B. Li, J. Mol. Catal. A: Chem. 147 (1999) 173.
- [22] R.-M. Wang, H.-X. Feng, Y.-F. He, C.-G. Xia, J.-S. Suo, Y.-P. Wang, J. Mol. Catal. A: Chem. 151 (2000) 253.
- [23] B.B. De, B.B. Lohray, P.K. Dhari, Tetrahedron Lett. 34 (1993) 2371.
- [24] C. Bowers, P.K. Dutta, J. Catal. 122 (1990) 271.
- [25] M.J. Sabater, A. Corma, A. Domenech, V. Fornes, H. Garcia, J. Chem. Soc. Chem. Commun. 14 (1997) 1285.
- [26] M.N.V. Ravi Kumar, React. Funct. Polym. 46 (2000) 1.
- [27] C.C. Guo, G. Huang, X.B. Zhang, D.C. Guo, Appl. Catal. A: Gen. 247 (2003) 261.
- [28] T. Vincent, E. Guibal, Ind. Eng. Res. Chem. 41 (2002) 5158.
- [29] L.M. Tang, M.Y. Huang, Y.Y. Jiang, Chin. J. Polym. Sci. 14 (1996) 57.
- [30] Y. An, D. Yuan, M.Y. Huang, Y.Y. Jiang, Macromol. Symp. 80 (1994) 257.
- [31] L.M. Tang, M.Y. Huang, Y.Y. Jiang, Macromol. Rapid Commun. 15 (1994) 527.
- [32] H.S. Han, S.N. Jiang, M. Huang, Y.Y. Jiang, Polym. Adv. Technol. 7 (1996) 704.
- [33] M.-Y. Yin, G.-L. Yuan, Y.-Q. Wu, M.-Y. Huang, Y.-Y. Liang, J. Mol. Catal. A. 147 (1999) 93.
- [34] F. Quignard, A. Choplin, A. Domard, Langmuir 16 (2000) 9106.
- [35] P. Buisson, F. Quignard, Aust. J. Chem. 55 (2002) 73.
- [36] Y. Chang, Y.P. Wang, Z.X. Su, J. Appl. Polym. Sci. 83 (2002) 2188.
- [37] J.J.E. Hardy, S. Hubert, D.J. Macquarrie, J. Wilson, Green Chem. 6 (2004) 53.
- [38] Y. Chang, Y. Wang, F. Zha, R. Wang, Polym. Adv. Technol. 15 (2004) 1.
- [39] W. Sun, C.G. Xia, H.W. Wang, NJ Chem. 26 (2002) 755.
- [40] H.W. Wang, W. Sun, C.G. Xia, J. Mol. Catal. A: Chem. 206 (2003) 199.

- [41] Jay F. Larrow, Eric N. Jacobsen, *J. Org. Chem.* 59 (1994) 1939.
- [42] X.D. Du, *Selective Epoxidation of Unfunctionalized Olefins Catalyzed by Unsymmetric Schiff-base Transition Metal Complex*, PhD Dissertation, Graduate School of Chinese Academy of Sciences, 1995.
- [43] W. Sun, *Chiral Salen Metal Complexes Catalyzed Asymmetric Reactions*, PhD Dissertation, Graduate School of Chinese Academy of Sciences, 2003.
- [44] Z.W. Yang, Q.X. Kang, H.C. Ma, C.L. Li, Z.Q. Lei, *J. Mol. Catal. A: Chem.* 213 (2004) 169.