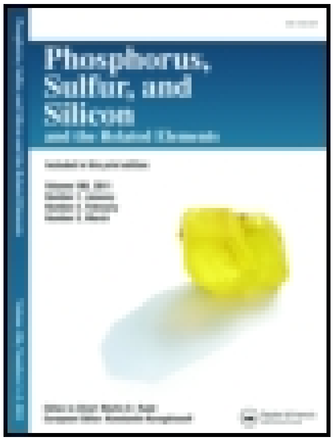
This article was downloaded by: [Uppsala universitetsbibliotek]
On: 19 November 2014, At: 05:04
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Aminopropyl group-modified SBA-15 covalent attachment Mn(salen) complexes as catalysts for styrene epoxidation

Lili Liu[a], Jianglei Hu[ab], Jiaojiao He[a], Haojie Lu[ab], Yong Xu[ab] & Fengwei Shi[a]

[a] School of Chemical Engineering, Changchun University of Technology, Changchun 130012, P. R. China

[b] Advanced Institute of Materials Science, Changchun University of Technology, Changchun 130012, P. R. China

Accepted author version posted online: 14 Nov 2014.

To cite this article: Lili Liu, Jianglei Hu, Jiaojiao He, Haojie Lu, Yong Xu & Fengwei Shi (2014): Aminopropyl group-modified SBA-15 covalent attachment Mn(salen) complexes as catalysts for styrene epoxidation, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2014.979983

To link to this article: http://dx.doi.org/10.1080/10426507.2014.979983

Disclaimer: This is a version of an unedited manuscript that has been accepted for publication. As a service to authors and researchers we are providing this version of the accepted manuscript (AM). Copyediting, typesetting, and review of the resulting proof will be undertaken on this manuscript before final publication of the Version of Record (VoR). During production and pre-press, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal relate to this version also.

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Aminopropyl group-modified SBA-15 covalent attachment Mn(salen) complexes as catalysts for styrene epoxidation

Lili Liu[a], Jianglei Hu[a,b1], Jiaojiao He[a], Haojie Lu[a,b], Yong Xu[a,b], Fengwei Shi[a*]

[a] *School of Chemical Engineering, Changchun University of Technology, Changchun 130012, P. R. China*

[b] *Advanced Institute of Materials Science, Changchun University of Technology, Changchun 130012, P. R. China*

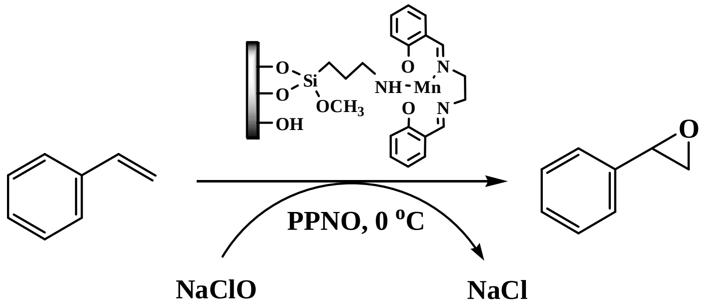
---

[1] Corresponding author. Tel. or Fax: +86-431-85717353.

E-mail address: hujl863@163.com.

Abstract

A series of aminopropyl group-modified ordered mesoporous silica materials impregnated with Mn(salen) was prepared using successive grafting procedures. The prepared composite catalysts were well-characterized by inductively coupled plasma atomic emission spectroscopy, Fourier transform infrared, UV–vis diffuse reflectance spectroscopy, X-ray diffraction analysis, and transmission electron microscopy in order to confirm the structure integrities of the Mn(salen) units after the incorporation, to evidence the formation of the covalent bond between the starting Mn(salen) units and the aminopropyl group-modified SBA-15 matrix in the presence of NaOH by abstraction of a molecule HCl. These heterogeneous catalysts exhibited comparable catalytic activity and selectivity to those of the homogeneous counterpart in the epoxidation of styrene by using NaClO as the oxidant. In addition, the effects of key reaction parameters, including the loadings of the neat Mn(salen), molar ratios of NaClO to styrene, and PPNO amount on the reactivity and selectivity, were also studied. Finally, the reusability of the prepared heterogeneous catalyst was evaluated.



Key words SBA-15; Mn(salen) complex; Heterogeneous; Styrene; Epoxidation

1. Introduction

Epoxides are a significant class of industrial chemicals that have been widely used as chemical intermediates in several fields, such as agriculture, industry and medical science, and catalytic epoxidation of olefins is of great importance for the formation of epoxides[1-3]. Metal(salen) complexes have been reported as active catalysts for the epoxidation of olefins[4-6]. Among all kinds of the metal(salen) complexes, Mn(salen) complexes exhibit excellent performance towards the target reactions[7-10]. However, the reactions generally proceed in homogeneous systems, and presented the major problems in separation and recycling at the end of process. Given the high value of the catalysts and the harm to the environment, the heterogenization of Mn(salen) complexes has received widespread attention due to its inherent advantages of easy separation, recycling, and better handling properties[11-13]. For this purpose, many strategies for the heterogenization of the homogeneous catalysts include immobilizing metal(salen) complexes on poly-meric organic materials such as resins, or polystyrene[14], then supported on inert porous solid such as alumina[15], and silica[10] or encapsulated in the pores of zeolite-Y[16]. Among them, there has been an enormous evolution in the strategies to heterogenize metal(salen) complexes into/onto inorganic supports or inorganic-organic hybrid supports and organic polymers, in which the host-guest interaction is either chemical or physical.

In the current work, we designed and prepared a series of catalytically active, selective, and stable Mn(salen)-containing composite catalysts by immobilizing the Mn(salen) unit onto the aminopropyl group-functionalized SBA-15 silica materials via the covalence of Mn centers in the Mn(salen) unit with nitrogen atoms of aminopropyl group-functionalized SBA-15 silica materials in the presence of NaOH by abstraction of a molecule HCl.

The prepared composite catalysts were well-characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES), Fourier transform infrared (FT-IR) spectroscopy, UV-vis diffuse reflectance spectroscopy (UV-vis/DRS), low-angle X-ray diffraction (LXRD) analysis, and transmission electron microscopy (TEM) in order to confirm the structure integrities of the Mn(salen) unit after the incorporation, to evidence the formation of the covalent bond between the starting Mn(salen) unit and the aminopropyl group-modified SBA-15 matrix. The resulting heterogeneous catalysts possess highly well-defined mesoporous structure. Meanwhile, the as-synthesized Mn(salen)-NH/SBA-15 materials showed efficient activity and selectivity for the catalytic epoxidation of styrene (Scheme 1). The influences of key reaction parameters, including the Mn(salen) loadings, axial ligand, molar ratios of NaClO to styrene, and reaction time were also studied. Finally, the reusability of the catalysts was evaluated.

2. Results and discussion

2.1 Characterization techniques

Low angle XRD (LXRD) patterns were obtained on a D/max-2200 VPC diffractometer using Cu*Ka* radiation. TEM images were obtained on a JEOL JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV. FT-IR spectra were recorded on a Nicolet Magna 560 IR spectrophotometer. UV–Vis diffuse reflectance spectra (UV–Vis/DRS) were recorded on a Cary 500 UV–Vis–NIR spectrophotometer with a frequency interval of 1 cm^{-1}. Loading of Mn(salen) was determined on a Leeman Prodigy Spec inductively coupled plasma atomic emission spectrometer (ICP-AES).

2.2 Characterization of catalyst

2.2.1 FI-IR

The FT-IR spectra of SBA-15, NH_2/SBA-15, Mn(salen) and Mn(salen)-NH/SBA-15(6.4) materials were presented in Figure 1. A pair of weak absorption peaks at 2985 cm^{-1} and 2937 cm^{-1} was ascribed to the symmetric and asymmetric of the saturation of C–H, manifesting that the modified aminopropyl groups successfully into silicon matrix surface (NH_2/SBA-15)[3]. From Figure 1, it can be seen that the heterogeneous catalyst displayed the similar vibrational absorption bands as the starting Mn(salen) complex. Concretely, the band at 1540 cm^{-1} and the peak at 542 cm^{-1}, attributed to the characteristic absorption peak and the stretching vibrations of the Mn–O bond of the complex can be observed in the heterogeneous catalyst Mn(salen)-NH/SBA-15(6.4)[17,18],demonstrating that the Mn(salen) complex was immobilized on the support.

2.2.2 UV-Vis/DRS

The characteristic UV-Vis/DRS spectra of homogeneous and heterogeneous Mn(salen) materials were presented in Figure S 1 (Supplemental Materials). It revealed that the characteristic absorption bands related to the starting Mn(salen) complexes were still found in the heterogeneous Mn(salen)-NH/SBA-15(6.4) material. That was to say, the Mn(salen) complex exhibited four absorption bands at 261 nm, 331 nm, 431 nm, and 518 nm, which were assigned to π–π^* transition of the phenyl ring on salen, n–π^* transition of azomethine C=N bond, charge-transfer between the Mn and ligand, and d–d transition of Mn(III), respectively[19,20] .The result implied that the primary structure of the starting Mn(salen) remained intact after the immobilization.

2.2.3 Low-angle of XRD

LXRD patterns of SBA-15, NH_2/SBA-15, and Mn(salen)-NH/SBA-15(6.4) materials were presented in Figure 2. The results showed that all of the materials exhibited three well-resolved peaks at 0.95, 1.69, and 1.96 deg, which were respectively indexed as the (100), (110), and (200) reflections of *p6mm* hexagonal symmetry. As for the three SBA-15 materials, their (100), (110), and (200) reflections still existed, but the peak intensities decreased in the order SBA-15 > NH_2-SBA-15 > Mn(salen)-NH/SBA-15(6.4). Compared with SBA-15 support values, decreased peak intensities for the Mn(salen)-NH/SBA-15(6.4) sample could be explained in term of the presence of high Mn(salen) unit and APS contents in the mesoporous Mn(salen)-NH/SBA-15(6.4) channels, which could partially disturb the assembly of the mesophase.

2.2.4 TEM

The ordered mesostructure of Mn(salen)-NH/SBA-15(6.4) material was further confirmed by TEM observation; some representative results were shown in Figure 3. Despite the aminopropyl groups functionalization of SBA-15 with the Mn(salen) units, the highly ordered mesostructure of SBA-15 was maintained over extensive regions of observation. The observation indicated that the prepared composite exhibited hexagonal lattice fringes with uniformly parallel cylindrical pore channels, meaning that the material possessed a two-dimensionally ordered hexagonal symmetry (p6mm) structure.

2.3 Catalytic activity studies

The catalytic performance of the prepared catalyst was studied by the catalytic epoxidation of styrene. In order to compare, that of the homogeneous Mn(salen) and silica support SBA-15 were tested under identical condition. The effect of various experiment parameters, including the loadings of the neat Mn(salen), the PPNO amount, and molar ratios of NaClO to styrene were studied and the situations were stated as follows.

2.3.1 Catalyst text

Before epoxidation reaction, the catalyst was activated at 373 K for 2 h. Catalytic epoxidation of styrene was carried out in a sealed round-bottom flask (25 mL) for 24 h under vigorous stirring at 273 K (Scheme 1). In a typical experiment, styrene (1.0 mmol), octane (internal standard, 1.0 mmol), 4-PPNO (0.3 mmol), CH_2Cl_2 (3 mL), aqueous NaClO solution (pH 11.3, 0.55 M, 2.0 mmol), and the catalyst powder (containing Mn(salen) 0.018 mmol). Changes of the concentrations of alkene and epoxide in the system were monitored quantitatively by a multicolumn Agilent Technologies 6890N gas chromatograph with thermal conductivity (TCD) and flame ionization (FID) detectors. The performance of the catalysts was evaluated by the yield of epoxide (Yield%), the selectivity to epoxide (Selectivity%), and the conversion of styrene (Conversion%). Herein, Yield% = $(N_Y/N_E) \times 100$, where N_Y and N_E are the number of moles of the epoxides yielded and expected; Selectivity% = Yield% /Conversion% × 100.

2.3.2 Effect of the different catalysts

The catalytic activity of a series of catalysts was compared and the results were described in the Table 1. The blank experiment was tested at first. Blank experiment showed that the SBA-15 support alone was inactive towards the styrene epoxidation (entry 1 in Table 1). However, significant conversion of styrene to styrene epoxide was found in the presence of homogeneous Mn(salen) complexes as well as heterogeneous Mn(salen) materials (entries 2-5 in Table 1). Moreover, in current catalytic system, styrene epoxide was the only product. The influence of Mn(salen) complex loadings on the catalytic activity of Mn(salen)-NH/SBA-15 materials were evaluated by the representative catalyst. Increased Mn(salen) loading from 3.5% to 7.1%, the yield of styrene epoxide increased from 47.2% to 89.2% for 24 h (entries 3-5 in Table 1). These results show that the reactivity increased when the Mn(salen) loading was increased from 3.5 to 6.4%; further increasing the Mn(salen) loading to 7.1% did not have any effect on the reactivity.

Hence, in the following catalytic tests, the most active catalyst, Mn(salen)-NH/SBA-15(6.4), was selected to study the influence of key reaction parameters on the catalytic activity, selectivity, recovery, and reuse of the immobilized Mn(salen) complexes.

2.3.3 Effect of the axial ligand (PPNO)

The contribution of PPNO to the homo- or heterogeneous Mn(salen) complex-catalyzed styrene epoxidation reaction is studied and the results are summarized in Table S 1 (Supplemental Materials). It shows that PPNO applied in current catalytic system can obviously enhance the catalytic activity of both of the homogeneous and heterogeneous Mn(salen) complexes[3]. Under the same conditions, increased PPNO amount from 0 to 0.3 mmol, the yield of styrene epoxide increased from 2.8% to 88.9% (entries 3-6 in Table S 1 Supplemental Materials). But, further increasing the PPNO amount to 0.6 mmol did not have any effect on the reactivity.

2.3.4 Effect of molar ratio of NaClO to styrene

Epoxidation of styrene catalyzed by the Mn(salen)-NH/SBA-15(6.4) catalyst at the different molar ratios of NaClO to styrene in the reaction system was studied; the result is shown in Figure 4. It was found that the yield of styrene epoxide increased from 23.2 to 80.2 % as the molar ratio of NaClO to styrene increased from 1:1 to 4:1. This suggested that a suitable excess of oxidant could improve the catalytic activity and selectivity. However, the selectivity of styrene declined to 81.6% rapidly when the molar ratio of NaClO to styrene was 4:1, which was responsible for the open-ring or bond-broken reaction of styrene epoxides in the presence of excessive NaClO solution. Therefore, the molar ratio of NaClO to styrene should be controlled at 2:1, which was the first and foremost condition of high conversion and selectivity.

2.3.5 Effect of the reaction time

From the result displayed in Figure 5, one can see that the conversion of styrene as well as the yield of epoxide increased rapidly at the beginning of the reaction. After the reaction proceeded for 10 h, the reaction rate began to slow down. The reaction proceeded more slowly on further increasing the reaction time. However, the selectivity to epoxide remained unchanged basically throughout the entire reaction procedure. When the time was 24 h, the conversion and yield were both up to 88.9%. Moreover, the selectivity kept at 100% during the whole reaction.

To confirm the absence of the active site (Mn(salen)) leaching into the reaction medium during the catalytic course, we carried out the reaction at 273 K for 3 h, and then we removed the catalyst by filtration. The catalyst-free reaction liquor was allowed to react further for 24 h; however, no further conversion of styrene was detected, consistent with a stable heterogeneous catalyst (Figure 5). Meanwhile, the catalyst-free reaction solutions were analyzed by ICP-AES to estimate the drop of Mn(salen). As expected, Mn was hardly detected in the catalyst-free reaction solution.

2.3.6 The reusing of the heterogeneous Mn(salen) catalyst

Alkene epoxidation catalyzed by Mn(salen) complexes in the presence of strong oxidizing reagents often suffered from deactivation due to the ligand degradation. Therefore, the catalytic stability of heterogeneous Mn(salen) complexes was evaluated through three consecutive styrene epoxidation cycles catalyzed by Mn(salen)-NH/SBA-15(6.4) material. After the first run, the used catalyst was recovered by filtration and then washed thoroughly with dichloromethane. The results showed that the Mn(salen)-NH/SBA-15(6.4) catalyst retained most of its initial activity (Figure 6) after three consecutive styrene epoxidation cycles: the yield of styrene epoxide was 88.9%, 85.0%, and 79.6%, respectively, for the 1st, 2nd and 3rd run. The results indicated that the prepared heterogeneous catalyst had excellent thermal stability. The decline of conversion and yield may be the loss of catalyst during the washing and recycling process.

2.3.7 Reaction mechanism consideration

Taking into account the product yielded (styrene epoxide) in the current catalytic system, the reaction mechanism was proposed. In the first step, oxygen transferred from a donor (NaClO) to Mn center of Mn^{III}(salen)-NH/SBA-15 occurred, leading to a higher valent oxomanganese(salen)(V) active species, $O{=}Mn^{V}$(salen)-NH/SBA-15[21]. In the second step, the oxygen atom of $O{=}Mn^{V}$(salen)-NH/SBA-15 species attacked nucleophilically on the carbon atom with lower electron cloud density of C=C bond within the alkenes, leading to the formation of radical intermediate[22]. In the third step, the radical intermediate was directly collapsed and formed the epoxide. Simultaneously, the catalyst restored its initial state due to the loss of an oxygen atom.

3. Experimental

3.1 Materials

4-phenylpyridine N-oxide, and Pluronic P123 (MW=5800) was purchased from sigma-aldrich (Shanghai), 3-aminopropyl-triethoxysilane (98.0%) was purchased from Aladdin Chemistry Co. (Shanghai). Styrene (99.0%) and Tetraethyl orthosilicate (TEOS, 98.0%) were purchased from Tianjin Fuchen Chemical Reagent Factory (China). All other chemicals were analytical grade and were purchased from Beijing Fine Chemical Co. (China) and used without further purification.

3.2 Catalyst preparation

3.2.1 Synthesis Mn(salen) complex

Homogeneous Mn(salen) complex was synthesized following the procedures illustrated in Scheme 2a. Preparation of Mn(salen) complexe was carried out by the literature methods[23,24].

3.2.2 Preparation of silica support SBA-15

Highly ordered mesoporous SBA-15 was synthesized using a modified procedure based on the literature method[25]. In a typical synthesis, P123 (1.0 g) was dissolved in distilled water (15 mL) to which aqueous HCl solution (2 mol·L^{-1}, 30 mL) was added under stirring at 308 K for 3 h, and then TEOS (4.0 g) was added into the above solution under stirring at 308 K for 20 h. The resulting mixture was aged under static hydrothermal conditions at 353 K for 24 h. The separated white product powder was washed with distilled water for three times, and then it was dried for 48 h at 373 K. Surfactant template P123 was removed from the product by extracting with ethanol in the presence of HCl (2 M). After being dried at 373 K for 24 h, the final product was formed and denoted as SBA-15.

3.2.3 Preparation of amine-functionalized SBA-15 (NH_2/SBA-15)

3-Aminopropyl-trimethoxysilane (APS, 1 mL) was dispersed into a suspension including ethanol (50 mL) and SBA-15 (1 g). The mixture was stirred vigorously at room temperature for 24 h, and then the product was recovered by centrifugation after washing with ethanol and diethyl ether, respectively[26,27]. The final product was formed and denoted as NH_2-SBA-15. The preparation procedure was shown in Scheme 2b.

3.2.4 Preparation of heterogeneous Mn(salen) catalysts

The preparation procedure was shown in Scheme 2. The mixture of Mn(salen) (0.2-0.5 g) and modified support (NH_2/SBA-15, 0.5 g) were added to THF (25 mL) for 24 h in the presence of NaOH (0.6-1.6 mmol) at room temperature[28].The resulting solid product was filtrated, washed thoroughly with THF then ethanol for three times, and the separated brown powder was dried in vacuum at 353 K. The final product was denoted as Mn(salen)-NH/SBA-15-x (where x presents Mn(salen) loading amount (wt.%) in the product, which was determined by a Leeman Plasma Spec (I) ICP-AES.).

4. Conclusions

A series of ordered mesoporous Mn(salen)-NH/SBA-15 composite catalysts for epoxidation of styrene was developed. The structures of the starting Mn(salen) unit was maintained in the composite catalysts, and the interaction between the Mn(salen) unit and the aminopropyl group-functionalized SBA-15 material is the Mn-N covalent bond in the presence of NaOH. Under identical reaction conditions, this heterogeneous catalyst showed comparable catalytic activity and selectivity to the corresponding homogeneous counterpart towards the epoxidation of styrene into epoxide using NaClO as oxidant. Meanwhile, factors including the loadings of the Mn(salen), molar ratios of NaClO to styrene, PPNO amount, and reaction time also had obvious influences on the reactivity and selectivity. Importantly, the prepared Mn(salen) complexes can be reused at least three times without obvious loss of activity.

Acknowledgments

This work was supported by the Natural Science Fund Council of China (21203013).

References

[1] Kamata, K.; Yonehara, K.; Sumida, Y.; Yamaguchi, K.; Hikichi, S.; Mizuno, *N. Science*. **2003,** 300, 964-966.

[2] Palucki, M.; McCormick, G. J.; Jacobsen, E. N. *Tetrahedron Lett.*, **1995,** 36, 5457-5460.

[3] Hu, J. L.; Wu, Q. Y.; Li, W.; Ma, L.; Su, F.; Guo, Y. H.; Qiu, Y. Q. *ChemSusChem*. **2011,** 4, 1813-1822.

[4] Cheung, K. C.; Wong, W. L.; Ma, D. L.; Lai, T. S.; Wong, K. Y. *Coord. Chem. Rev*. **2007,** 251, 2367-2385.

[5] Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc*. **1990,** 112, 2801-2803.

[6] Parida, K. M.; Sahoo, M.; Singha, S. *J. Catal*. **2010,** 276, 161-169.

[7] Aerts, S.; Weyten, H.; Buekenhoudt, A.; Gevers, L. E. M.; Vankelecom, I. F. J.; Jacobs, P. A. *Chem. Comm*. **2004,** 710-711.

[8] Bigi, F.; Moroni, L.; Maggi, R.; Sartori, G. *Chem. Commun*. **2002,** 716-717.

[9] Zhang, H.D.; Li, C. *Tetrahedron*. **2006,** 62, 6640–6649.

[10] Hatefi, M.; Moghadam, M.; Sheikhshoaei, I.; Mirkhani, V.; Tangestaninejad, S.; Mohammadpoor-Baltork, I.; Kargar, H. *Appl. Catal. A:* **2009,** 370, 66-71.

[11] Dell'Anna, M. M.; Gallo, V.; Mastrorilli, P.; Romanazzi, G. *J. Molecules.* **2010,** 15, 3311-3318.

[12] Sellner, H.; Karjalainen, J. K.; Seebach, D. *Chem. Eur. J*. **2001,** 7, 2873-2887.

[13] Bhattacharjee, S.; Anderson, J. A. *Chem. Commun*. **2004,** 554-555.

[14] Maurya, M. R.; Kumar, A. *J. Mol. Catal. A: Chem*. **2006,** 250, 190-198.

[15] Salavati-Niasari, M.; Amiri, A. *Appl. Catal. A: Gen*. **2005,** 290, 46-53.

[16] Varkey, S. P.; Ratnasamy, C.; Ratnasamy, P. J. *Mol. Catal. A: Chem.* **1998,** 135, 295-306.

[17] Yang, H. Q.; Zhang, L.; Wang, P.; Yang, Q. H.; Li, C. *Green Chem*. **2009,** 11, 257-264.

[18] Choudary, B. M.; Ramani, T.; Maheswaran, H.; Prashant, L.; Ranganath, K. V. S.; Vijay Kumar, K. *Adv. Synth. Catal*. **2006,** 348, 493-498.

[19] Zhang, H. D.; Zhang, Y. M.; Li, C. *J. Catal*. **2006,** 238, 369-381.

[20] Crawford, S. M. *Spectrochim. Acta*, **1963,** 19, 255-270.

[21] Campbell, K. A.; Lashley, M. R.; Wyatt, J. K.; Nantz, M. H.; Britt, R. D. *J. Am. Chem. Soc.* **2001,** 123, 5710-5719.

[22] Linde, C.; Åkermark, B.; Norrby, P. O.; Svensson, M. *J. Am. Chem. Soc.* **1999,** 121, 5083-5084.

[23] Zhang, W.; Jacobsen, E.N. *J. Org. Chem*. **1991,** 56, 2296-2298.

[24] Amarasekara, A. S.; McNeal, I.; Murillo, J.; Green, D.; Jennings, A. *Catal. Comm*. **2008,** 9, 2437-2440.

[25] Zhao, D. Y.; Huo, Q. S.; Feng, J. L; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem*. Soc. **1998,** 120, 6024-6036.

[26] Utting, K. A.; Macquarrie, D. J. *New J. Chem*. **2000,** 24, 591-596.

[27] Hu, J. L.; Li, K. X.; Li, W.; Ma, F. Y.; Guo, Y. H. *Appl. Catal. A: Gen.* **2009,** 364, 211-220.

[28] Gong, B. W.; Fu, X. K.; Chen, J. X.; Li, Y. D.; Zou, X. C.; Tu, X. B.; Ding, P. P.; Ma, L. P. *J. Catal*. **2009,** 262, 9-17.

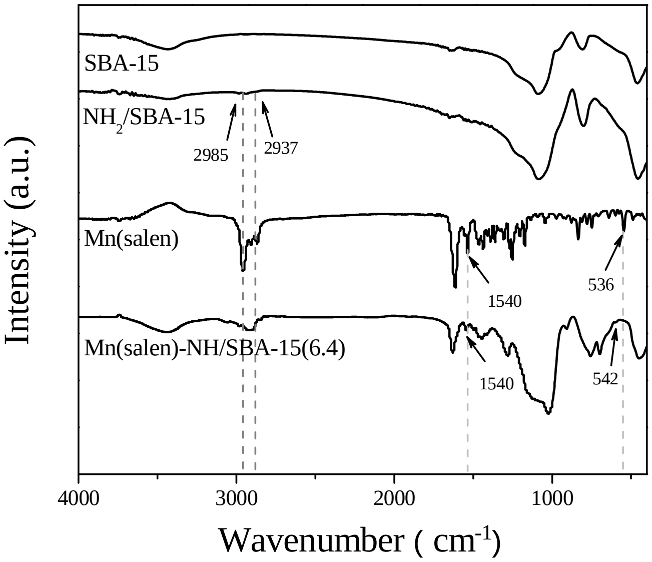


Figure 1 FT-IR spectra of SBA-15, NH_2/SBA-15, Mn(salen) and Mn(salen)-NH/SBA-15(6.4) materials.

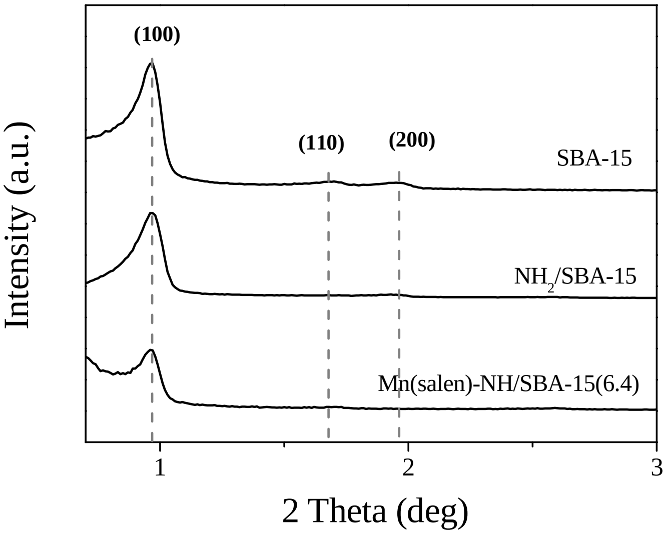


Figure 2 LXRD patterns of SBA-15, NH$_2$/SBA-15 and Mn(salen)-NH/SBA-15(6.4) materials.

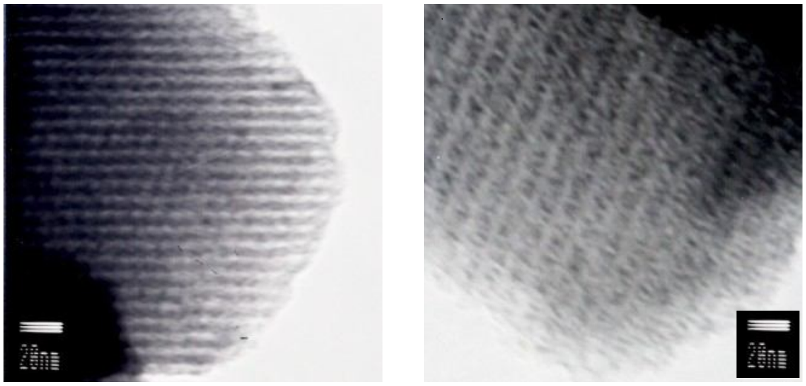


Figure 3 Transmission electron micrographs of Mn(salen)-NH/SBA-15(6.4) material

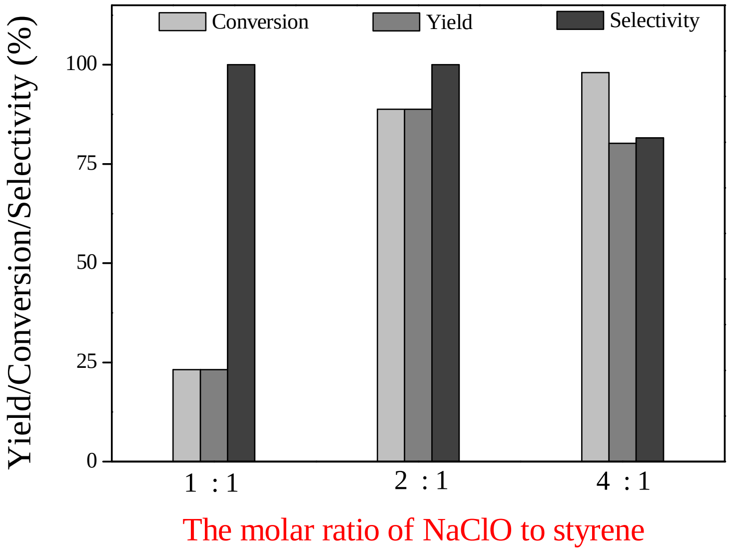


Figure 4 The effect of molar ratio of NaClO to Styrene on the catalytic activity and selectivity of Mn(salen)-NH/SBA-15 materials towards styrene epoxidation. Free Mn(salen) complex 0.018 mmol, CH_2Cl_2 3 mL, styrene 1.0 mmol, PPNO 0.3 mmol, n-octane 1.0 mmol, 273 K, 24 h.

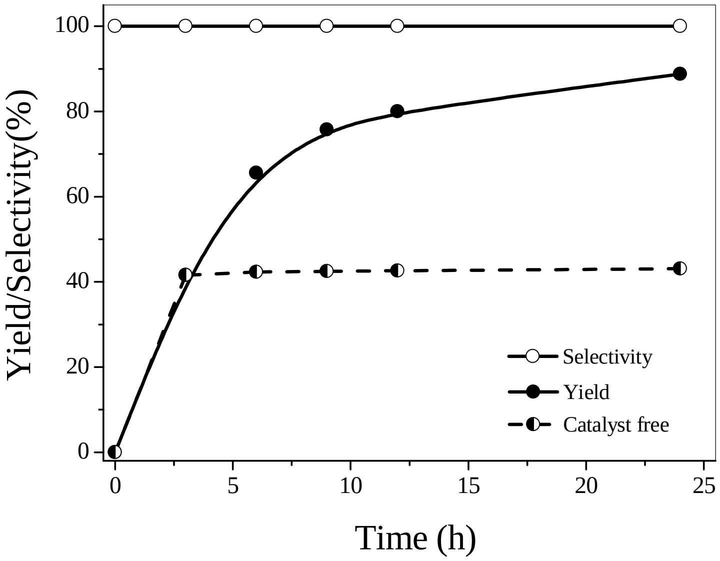


Figure 5 Time courses of epoxidation of styrene with NaClO to produce epoxide in the presence of Mn(salen)-NH/SBA-15(6.4) material. Free Mn(salen) complex 0.018 mmol, CH_2Cl_2 3 mL, styrene 1.0 mmol, NaClO 2.0 mmol, PPNO 0.3 mmol, n-octane 1.0 mmol, 273 K, 24 h.

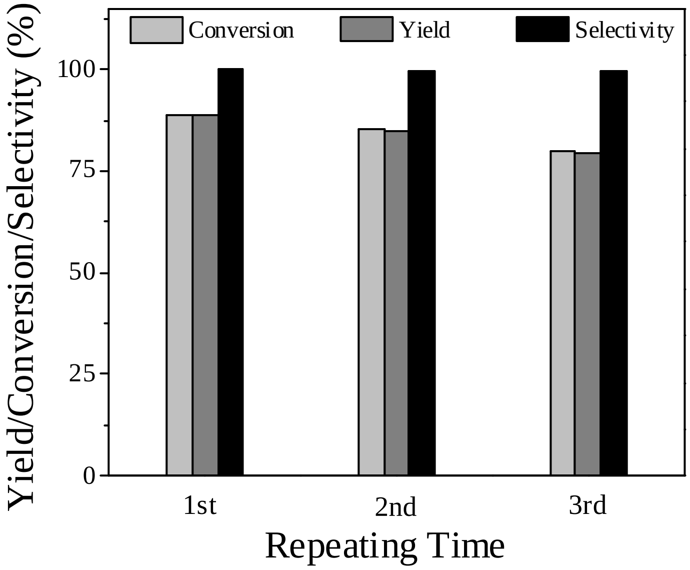
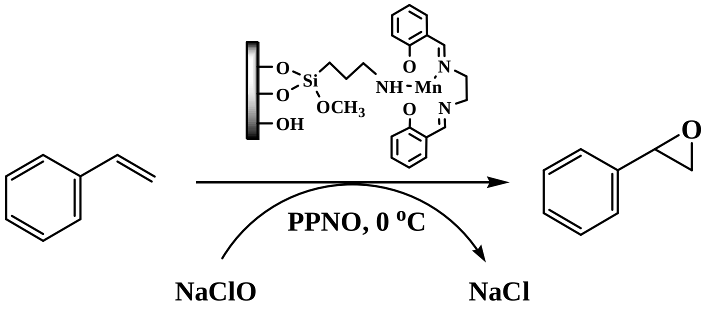
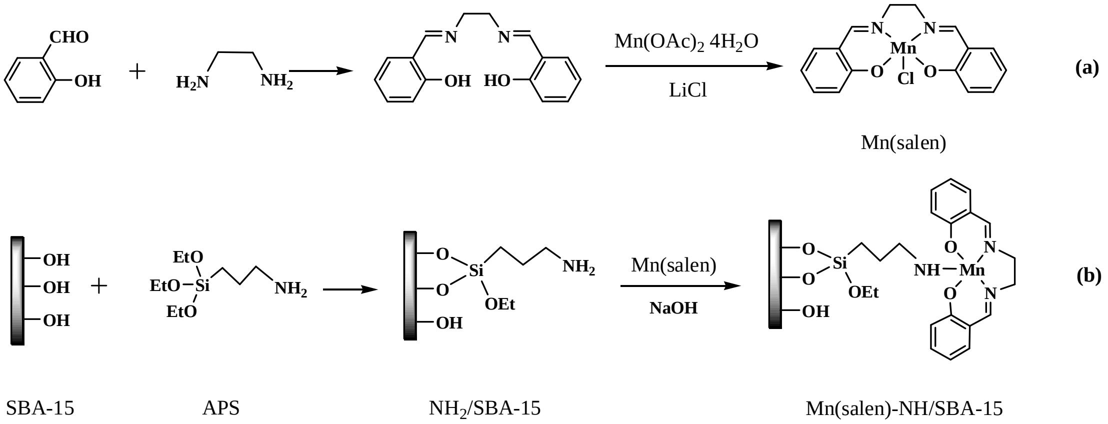


Figure 6 Recyclability of the Mn(salen)-NH/SBA-15(6.4) material towards the styrene epoxidation reaction. Free Mn(salen) complex 0.018 mmol, CH_2Cl_2 3 mL, styrene 1.0 mmol, NaClO 2.0 mmol, PPNO 0.3 mmol, n-octane 1.0 mmol, 273 K, 24 h.



Scheme 1 Reaction of oxidation of styrene to produce styrene epoxide with NaClO catalyzed by Mn(salen)-NH/SBA-15 materials.



Scheme 2 Pathway of the prepared of heterogeneous catalyst Mn(salen)-NH/SBA-15.

Table 1 Effect of various catalysts on the catalytic activity and selectivity of Mn(salen)-NH/SBA-15 materials towards styrene epoxidation.

Entry	Catalyst	Conversion (%)	Yield (%)	Selectivity (%)
1	SBA-15	–	–	–
2	Mn(salen)	94.6	94.6	100
3	Mn(salen)-NH/SBA-15(3.5)	47.2	47.2	100
4	Mn(salen)-NH/SBA-15(6.4)	88.9	88.9	100
5	Mn(salen)-NH/SBA-15(7.1)	89.2	89.2	100

Free Mn(salen) complex 0.018 mmol, CH_2Cl_2 3 mL, styrene 1.0 mmol, NaClO 2.0 mmol, PPNO 0.3 mmol, n-octane 1.0 mmol, 273 K, 24 h.