

Preparation of encapsulated and anchored alanine–salicylaldehyde Schiff base Mn(III) (Sal–Ala–Mn) complexes by sol–gel method and their performance in aerobic epoxidation of cyclohexene

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Abstract

Alanine–salicylaldehyde Schiff base Mn(III) complex was entrapped into SiO₂ matrix by direct physical encapsulation and copolymerization of the functionally modified complex and tetraethoxysilane. The two heterogenized catalysts were characterized by FT-IR, XPS, N₂ adsorption and ICP, and their catalytic performance in the aerobic epoxidation of cyclohexene was investigated. The experimental results showed both that the catalysts had higher catalytic activity and better epoxide selectivity than the homogeneous catalyst. After six recycle runs, the anchored catalyst had 1.6% activity reduction while that of the physically encapsulated one was 12.1%. ICP analysis indicated that complex leaching took place for the physically encapsulated catalyst but no complex leaching was found for the anchored one. Thus, for the aerobic epoxidation of cyclohexene (2.5 ml) catalyzed by the anchored catalyst (0.01 mmol) in the presence of isobutraldehyde (isobutraldehyde:cyclohexene = 2:1) using acetonitrile (60 ml) as solvent at 35 °C for 6 h the conversion reached 99.6% with a selectivity of 88.2%. This catalyst can be reused by simple filtration up to six times, retaining 99.4% of the activity of the fresh catalyst.

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1. Introduction

Epoxides are versatile and important intermediates in organic synthesis and the production of fine chemicals because they easily undergo stereospecific ring-opening to form bi-functional compounds under mild conditions. Generally, they are prepared by epoxidation of alkenes in industry and laboratory. The epoxidation of alkenes is traditionally carried out with stoichiometric or more amount of oxidant such as H₂O₂, ROOH, RCO₃H, NaOCl, KHSO₅, NaIO₄ or PhIO, so-called single oxygen donor [1]. Unfortunately, these methods are either expensive or dangerous. Some of the processes also generate a large amount of waste. Therefore, developing green, selective and efficient catalysts for the aerobic epoxidation of

alkenes is of importance for both economic and environmental reasons. Great efforts have been made to develop homogeneous metal complex catalysts for the aerobic epoxidation of alkenes [2–5]. However, the disadvantages of difficult separation of the homogeneous catalyst from the reaction mixture make it impossible to use on a large scale. Since heterogenization of homogeneous catalysts is expected to overcome this problem, it has become an interesting area of research. Extensive investigation has been focused on the incorporation of metal complex catalysts onto or into inert supports such as molecular sieves, amorphous silica, and polymers [6–11]. The sol–gel technique is another way to heterogenize homogeneous metal complex catalysts. Generally, there are two principle methods for immobilizing metal complexes by the sol–gel technique: directly physical doping [12,13]; functional modification of the ceramic matrix by copolymerization with organometallic alkoxides [14]; here we call it the

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anchoring method. In this work we employed the two sol–gel methods for immobilizing the alanine–salicylaldehyde Schiff base manganese(III) complex. Their catalysis in aerobic epoxidation of cyclohexene was comparatively studied.

2. Experimental

2.1. Materials

Alanine, AR, and salicylaldehyde, AR, were purchased from Tianjin Guangfu Fine Chemical Institute, Tianjin, China. 1,3-Dicyclohexylcarbodiimide (DCC), 99%, isobutyraldehyde and cyclohexene were from Acros Organics and used directly. *N*-hydroxysuccinimide and 3-aminopropyltriethoxysilane were obtained from Aldrich and used without further purification. Tetraethoxysilane (TEOS) was supplied by Tianjin First Chemical Reagent Factory, and distilled prior to use.

2.2. Characterization of the catalysts

FT-IR spectra (KBr pellet) were recorded on a Bruker Vector 22 spectrophotometer. N_2 adsorption analysis was measured on a Micromeritics ASAP 2010 Sorptometer. Prior to analysis, all samples were dried at 110 °C for 15 h. From the isotherm, BET surface area and pore volume were calculated. XPS spectra were recorded on a PHI 15300 ESCA instrument under vacuum 10^{-7} Pa and the Mg $K\alpha$ laser. The Mn content of the catalysts was determined by an ICP-900 (N + M) spectrophotometer, T J A Company, USA.

2.3. The analysis of the products

Reaction products were analyzed on a Shandong Lunan Ruihong Gas Chromatograph, SP-6800A, equipped with an SE 30 capillary column, 30.0 m \times 0.25 mm. The products were also characterized by Trace-DSQ GC–MS system with a CP Sil CB-MS capillary column, 30 m \times 0.25 mm \times 0.25 μ m, Thermo Electron Cooperation, USA.

2.4. Synthesis of Sal–Ala–Mn complex

Sal–Ala Schiff base ligand was prepared as described previously [15] from alanine and salicylaldehyde. The Sal–Ala–Mn complex was synthesized by the reported method [16].

2.5. Physical encapsulation of the complex

An amount of 0.25 g of Sal–Ala–Mn was dissolved in 30 ml of TEOS and 10 ml of methanol at 60 °C under stirring. Then 14.5 ml of water was added into the mixture to

obtain a homogeneous solution. To the solution, concentrate hydrochloric acid was introduced to adjust the pH to 4, which was determined using a calibrated pHS-2C pH meter equipped with E-201-C and 65-1AC combination pH electrodes. The stirring was continued under 60 °C until gelation was completed. Then the catalyst was dried at 80 °C until a constant weight was obtained. The gel was washed with water until the pH of the filtrate increased to 7. Then it was extracted with methanol in a Soxhlet extractor for 6 h. The content of Mn was determined by ICP.

2.6. Anchoring encapsulation of the complex

One gram of Sal–Ala Schiff base (A) was dissolved in absolute ethanol. Stoichiometric amount of H_2SO_4 was added dropwise and the solution filtrated to remove $KHSO_4$ a few minutes later. Then 0.5 g of *N*-hydroxysuccinimide and 1 g of DCC was added to the filtrate. After stirred for 24 h, the mixture was filtrated. The solvent was distilled off from the filtrate and a pale-yellow solid product (B) was obtained. B was dissolved in absolute ethanol and 0.96 g of 3-aminopropyltriethoxysilane was added into the mixture. After the mixture was stirred for 2 days, ethanol was distilled off. Tetrahydrofuran was added to dissolve the product and precipitate the *N*-hydroxysuccinimide. The precipitate was removed by filtration and tetrahydrofuran was distilled off from the filtrate to produce solid C. To the ethanol solution of C was added 0.58 g of $Mn(OAc)_2 \cdot 4H_2O$. After the mixture was refluxed for 3 h, 0.1 g of LiCl was added. The mixture was refluxed for further 2 h at 80 °C under O_2 and then cooled by ice. The solid D was collected by filtration. Add 0.96 g of solid D into the mixture of 43 ml of methanol and 24 ml of TEOS. To the solution 14 ml of water was added. Concentrated hydrochloric acid was used to regulate the pH to 3. The mixture was stirred until gelation was complete. The other procedures were the same as those in physical encapsulation.

2.7. Catalytic reactions

In a typical experiment, 0.01 mmol of catalyst (corresponding to 0.0531, 0.220 and 0.175 g of the homogeneous, physically encapsulated and anchored catalyst, respectively), 2.5 ml of cyclohexene, 4.6 ml of isobutyraldehyde, and 60 ml of acetonitrile were loaded into a 100 ml three-necked flask. The mixture was stirred and heated to 35 °C, and then air was bubbled for 6 h. The reaction mixture was analyzed by gas chromatography.

3. Results and discussion

3.1. Synthesis and characterization of the catalysts

We first prepared the homogeneous catalyst Sal–Ala–Mn as described in Ref. [16]. Its structure is shown in Fig. 1.

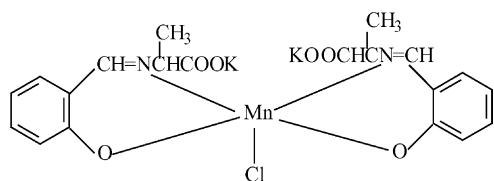


Fig. 1. The structure of Sal–Ala–Mn.

This complex was physically encapsulated into the SiO_2 by sol–gel process. This process is simple and straightforward: the complex was added to the TEOS polymerization mixture catalyzed by acid; when the polycondensation was completed, the complex was entangled in the SiO_2 polymeric network. The encapsulation conditions are mild, which can ensure the stability of the complex in the process. The FT-IR spectra of the neat complex (a) and the physically encapsulated Sal–Ala–Mn (b) are shown in Fig. 2. It is concluded that the peaks in spectrum b at the frequencies of 1637, 1509, and 1400 cm^{-1} , which are assigned to $\nu_{\text{C}=\text{N}}$, vibration of the skeleton of the phenyl group, and ν_{COO^-} , respectively, are due to the complex. However, it is not fully convincing that the complex is entrapped in the matrix because not all the peaks of the neat complex appeared. No satisfactory spectrum of the encapsulated complex catalyst was obtained although we tried several times. The reason is that the content of the complex is so low that its absorption peaks are masked by the strong background peaks of the SiO_2 matrix. To confirm that the complex was indeed entrapped in the matrix, we employed ICP to analyze the content of Mn in the catalyst. The result showed the content of Mn is 0.25%. Because the catalyst was extracted with methanol thoroughly, no contaminated complex on the matrix was left, and the Mn content should come from the complex entrapped in the matrix.

The preparation of anchored catalyst was carried out as shown in Scheme 1. We used concentrated H_2SO_4 to transform COOK to COOH. A typical method for the synthesis of polypeptide was employed to combine the acidified ligand with triethoxypropylsilanyl by an amide bond. The carboxy group was condensed with *N*-hydroxysuccinimide first in the presence of DCC to give the active ester, which smoothly reacted with the amino group of 3-aminopropyltriethoxysilane to generate an amide bond in mild conditions. This is important for ensuring the stability of Schiff base in all the process. By the coordination of the Schiff base with Mn^{3+} , the complex was stabilized in aqueous acidic conditions employed in the sol–gel process. The anchored catalyst was finally prepared by the copolymerization of TEOS with the complex with a triethoxypropylsilanyl functional group by the sol–gel technique (Scheme 1).

In the preparation procedures, the intermediates were followed by FT-IR shown in Fig. 3. Comparison of the spectra of A and B shows that several additional peaks appeared in that of B. The two peaks at 2929 and 2851 cm^{-1} are derived from $-\text{CH}_2-$ in the moiety of succinimide. The bands from 1700 to 1750 cm^{-1} are due to the stretching vibrations of the two kinds of carbonyl in the structure of B. The peak at 1781 cm^{-1} has been attributed to stretching vibration of the O–N bond. The disappearance of the peaks at 1781 and 1736 cm^{-1} in the spectrum of C clearly indicates that the *N*-oxysuccinimide moiety is replaced by the triethoxysilanylpropyl amino group. The remaining peaks at 2929 and 2851 cm^{-1} are due to $-\text{CH}_2-$ in the propylene stretching vibrations. The bands between 1400 and 1800 cm^{-1} in the spectrum of the complex (D) are assigned to the combination of the vibrations of $\text{C}=\text{N}$, $\text{CNH}_2=\text{O}$ and C–N in the complex. The spectrum of the anchored catalyst (E) is also given in Fig. 2. The peaks at the frequencies of 1637 and 1400 cm^{-1} , which are assigned to $\nu_{\text{C}=\text{N}}$, and $\nu_{\text{C}=\text{N}}$, respectively, are due

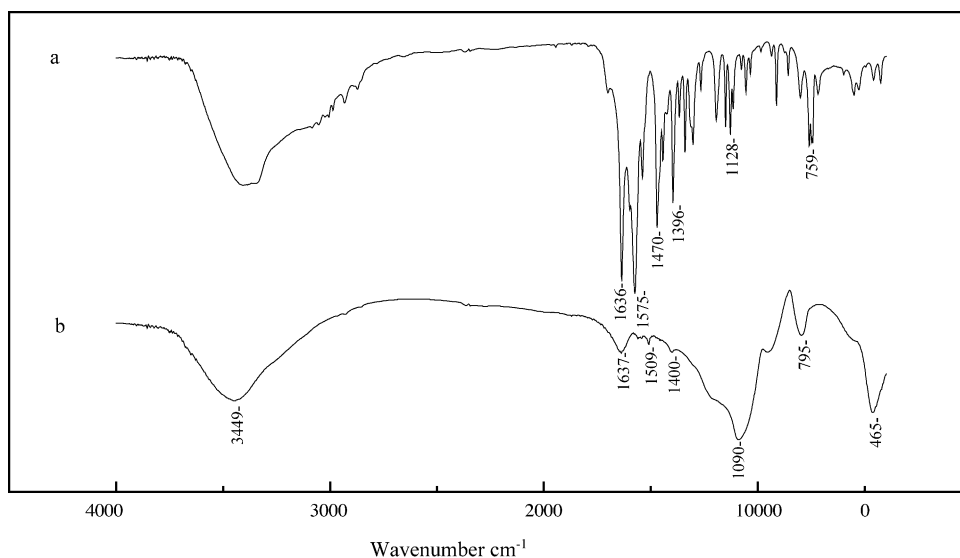
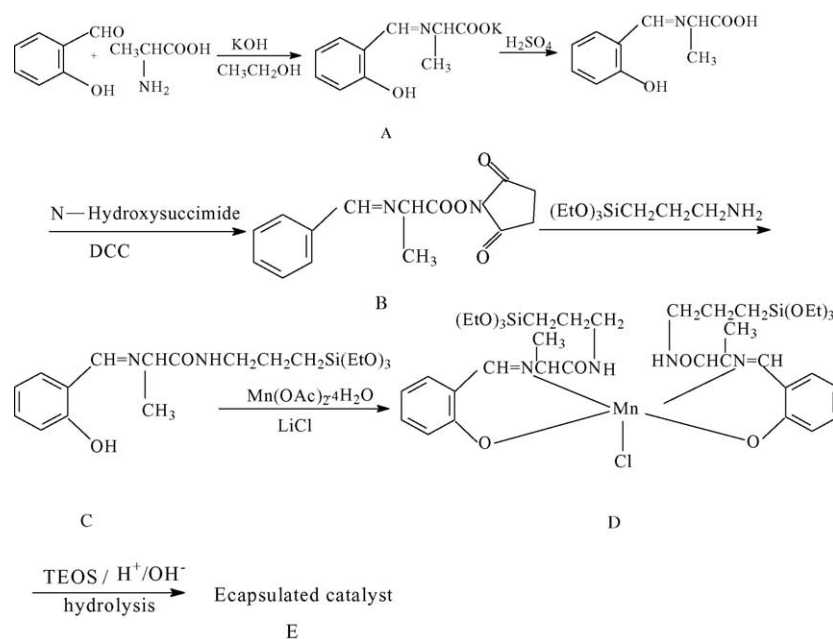


Fig. 2. The FT-IR spectra of the neat complex (a) and physically encapsulated catalyst (b).



Scheme 1. The process for preparing the anchored catalyst.

to the anchored complex. The peaks at 1085 and 959 cm^{-1} are due to the vibrations of Si–O–Si and Si–OH, respectively. The large difference in intensity between them indicates that the copolymerization goes well. The complex is anchored and entrapped in the SiO₂ matrix.

3.2. The content of Mn

The Mn content of both heterogenized catalysts was determined by ICP analysis after the samples were dissolved in

HF. Table 1 presents the Mn content of the two fresh catalysts and the recycled ones. The Mn content of both the catalysts is low. The low content of Mn is due to the low solubility of the complex in the mixture during the sol–gel process.

3.3. XPS spectra

Both of the heterogenized catalysts were also characterized by XPS. The spectra are given in Fig. 4. The binding energies of Mn in the physically encapsulated catalyst and the anchored one are 643.7 and 643.0 eV , respectively. This indicates the oxidation state of Mn ion in both of the catalysts is +3. The difference in the binding energy between them is the result of the anchored ligand strongly coordinating with Mn³⁺ compared to the free one. The strong coordination ability can increase the electron density around the Mn ion, which decreases the binding energy of the ion. After the first and sixth runs, the binding energy did not change, indicating the complexes were stable in the catalytic reaction process.

3.4. Catalytic performance

For fully understanding catalysis of the anchored catalyst, the parameters influencing its catalytic property were

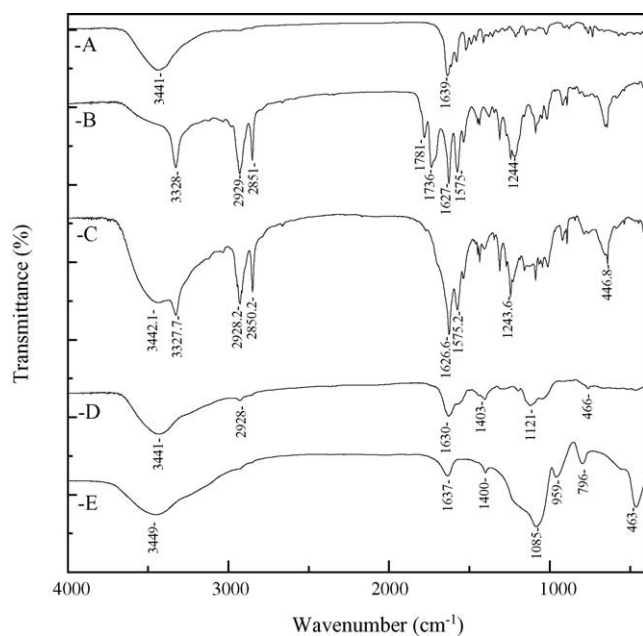


Fig. 3. The FT-IR spectra of A–E.

Table 1
The Mn content of the catalysts

Catalyst	Sample	Content of Mn (%)
Physically encapsulated one	Fresh	0.25
	After first run	0.19
	After sixth run	0.16
Anchored one	Fresh	0.33
	After first run	0.32
	After sixth run	0.33

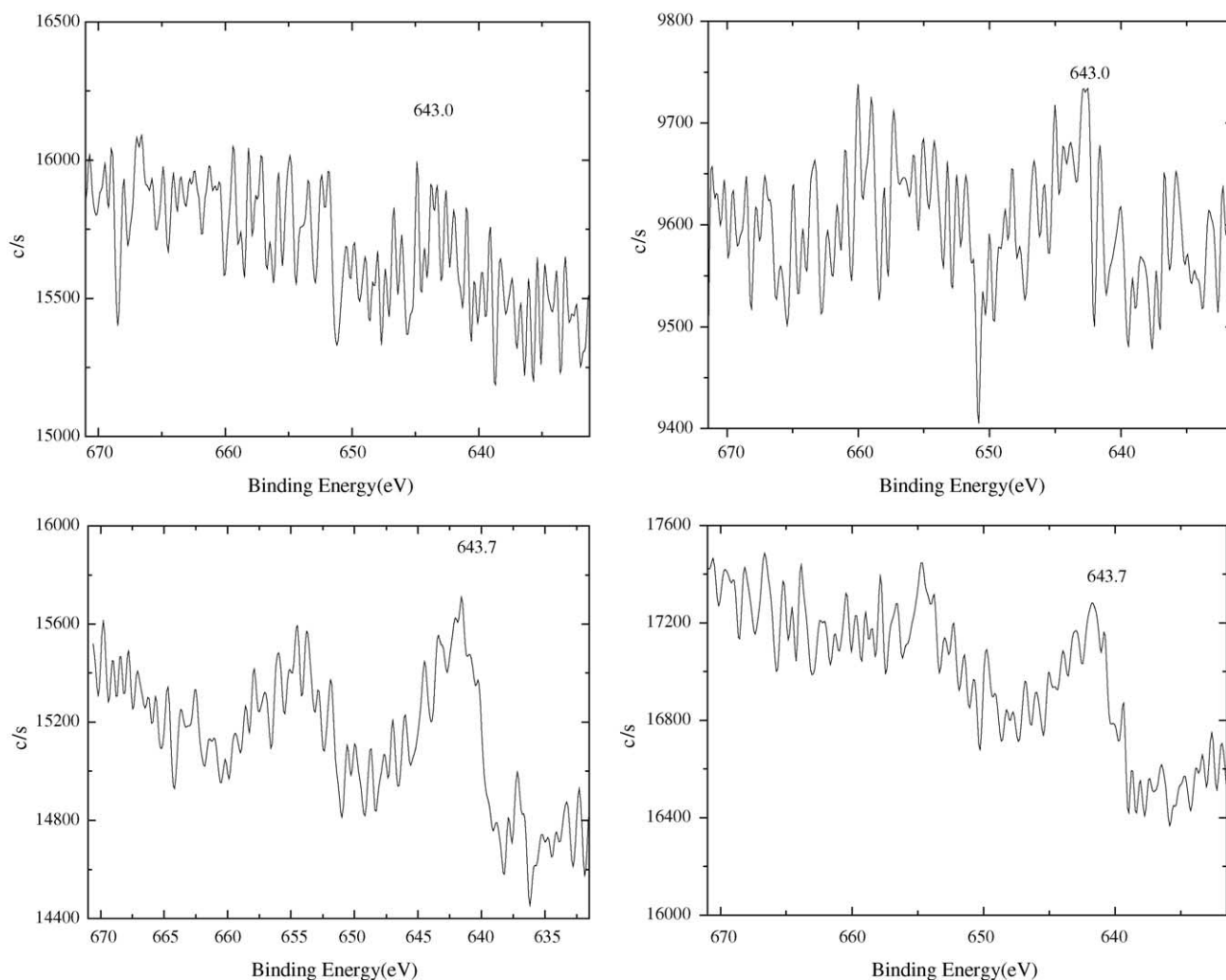


Fig. 4. The XPS spectra of catalysts before and after catalytic run. (a) Fresh anchored catalyst, (b) anchored catalyst after sixth run, (c) fresh physically encapsulated catalyst, (d) physically encapsulated catalyst after 1 run.

investigated. The results are presented in Table 2. It was shown that both the cyclohexene conversion and the epoxide selectivity increased sharply with time in the first 6 h. The conversion of cyclohexene was 96.3% and the epoxide selectivity reached a maximum of 77.2% after 6 h. Then the increase in the conversion became slow and the epoxide selectivity decreased. For determining the reason of the selectivity reduction, GC–MS was employed to analyze the reaction mixture. We found besides the target cyclohexene epoxide, several by-products including 2-cyclohexene-ol, 2-cyclohexene-1-one, and 1,2-cyclohexanedione were also formed. 2-Cyclohexene-ol and 2-cyclohexene-1-one were also observed by other researchers in the oxidation system free of isobutyraldehyde [17]. So we concluded that the epoxide selectivity is reduced for the following reasons. First the epoxide is obtained according to the mechanism given by Kureshy [18]. After the reaction materials enter into the matrix of the heterogenized catalyst, isobutyraldehyde reacts with the complex to initiate the radical chain process by generating an acyl radical, which reacts with molecular oxygen

to give an acylperoxy radical. The acylperoxy radical acts as a carrier in a chain mechanism by reacting with another isobutyraldehyde molecule to give a peroxy acid, with a concomitant generation of an acyl radical. The peroxy acid then reacts with catalyst to form a high valent metal-oxo intermediate, which on the approach of cyclohexene gives the epoxide. At the same time, the Schiff base Mn(III) complex can also catalyze the cyclohexene oxidation by oxygen to 2-cyclohexene-ol, 2-cyclohexene-1-one [17] and H₂O. Then H₂O react with epoxide to give 1,2-cyclohexanediol, which is easily converted to 1,2-cyclohexanedione by oxygen.

The temperature had no remarkable effect on the conversion of cyclohexene in the range from 25 to 55 °C. However the epoxide selectivity strongly depended on the temperature. The selectivity increased from 74.3 to 79.3% while the temperature was elevated from 25 to 35 °C. Then it decreased sharply to 60.7% at 55 °C, which indicated higher temperature could enhance the oxidation and ring opening reactions.

It is obvious more amount of catalyst can accelerate the epoxidation rate of cyclohexene. In Table 2 we can see the

Table 2
Epoxidation of cyclohexene by anchored catalyst under different conditions^a

Effect	Time (h)	Temperature (°C)	Catalyst weight (g)	Molar ratio ^b	Conversion (%)	Epoxide selectivity (%)
Time	2	25	0.200	2	36.2	69.4
	4	25	0.200	2	58.0	72.2
	6	25	0.200	2	96.3	77.2
	8	25	0.200	2	98.2	76.6
Temperature	6	25	0.200	2	96.3	74.3
	6	35	0.200	2	98.1	79.3
	6	45	0.200	2	98.5	62.9
	6	55	0.200	2	97.7	60.7
Catalyst weight	6	35	0.150	2	90.7	73.5
	6	35	0.175	2	97.3	80.0
	6	35	0.200	2	98.1	79.3
	6	35	0.225	2	98.7	75.0
Molar ratio ^b	6	35	0.175	1	73.7	72.8
	6	35	0.175	1.5	99.5	75.8
	6	35	0.175	2	97.3	80.0
	6	35	0.175	2.5	96.0	80.0

^a Solvent is acetonitrile, 60 ml.

^b The molar ratio of isobutyraldehyde to cyclohexene.

conversion increased to 97.3% and the epoxide selectivity reached the maximum of 80.0% when 0.175 g of the catalyst was loaded. When the catalyst weight was more than 0.175 g, the conversion increased slightly but the epoxide selectivity decreased. This phenomenon supports the idea that the Schiff base complexes can catalyze the aerobic oxidation of olefins to derivatives of propenol [17] in the absence of isobutyraldehyde. Here the excess catalyst accelerated the oxidation of cyclohexene to 2-cyclohexene-ol.

The molar ratio of isobutyraldehyde to cyclohexene is another key parameter, which influences the aerobic epoxidation of olefins. In the experiment the best conversion of 99.5% with an epoxide selectivity of 75.8% was obtained at the molar ratio of 1.5. The highest selectivity was 80.0% while the molar was 2 or more.

From the above results we conclude that the optimized conditions are as follows: the reaction time is 6 h, reaction temperature is 35 °C, catalyst weight is 0.175 g (1.0×10^{-5} mol), isobutyraldehyde:cyclohexene is 2:1, cyclohexene is 2.5 ml, acetonitrile is 60 ml. Under these conditions the conversion of cyclohexene is 97.3% and the epoxide selectivity is 80.0%.

After the optimized conditions were obtained for aerobic epoxidation of cyclohexene of the anchored catalyst, the catalytic performance of the two heterogenized catalysts and the homogeneous complex were studied by running the epoxidation reaction of cyclohexene under the same conditions. Table 3 presents the experimental results. The heterogenized catalysts were active in the epoxidation reaction of cyclohexene. The physically encapsulated catalyst had slightly lower conversion and the anchored catalyst had higher conversion than the homogeneous complex. Both of the heterogenized catalysts had much higher epoxide selectivity than the homogeneous one. As in other systems [19], the higher conversion and selectivity could be explained by assuming that in the homogeneous condition the reaction rate is suppressed by

Table 3
The catalytic performance of the different catalysts

Catalyst	Conversion (%)	Selectivity of epoxide (%)
Homogeneous	89.3	73.2
Physically encapsulated	87.8	80.46
Anchored	99.6	88.21

Reaction conditions: catalyst 0.01 mmol, cyclohexene 2.5 ml, isobutyraldehyde:cyclohexene = 2:1, acetonitrile 60 ml, reaction temperature 60 °C, reaction time 6 h.

the poor solubility of the complex in the solvent and by self-degradation. The other reason is that the site isolation effect makes the complex in a molecularly dispersed form, which causes no self-degradation to take place.

One reason for the lower activity and epoxide selectivity of the physically encapsulated catalyst than the anchored one may be the lower surface area and average pore diameter of the matrix (see Table 4). The other reason is the leaching of the catalyst in the reaction (XPS, ICP), which makes the complex partly enter into the solution. In other words, the conversion and selectivity are the combination result of heterogeneous and homogeneous catalysis.

3.5. Recycle test

One of the advantages of heterogenized catalysts is their recyclability. Both of the heterogenized catalysts were used in subsequent catalytic runs, and the results are given in Table 5. It clearly shows that the activity of the anchored

Table 4
N₂ adsorption results of the two heterogenized catalysts

Catalyst	BET (m ² /g)	Pore volume (m ³ /g)	Average pore diameter (Å)
Physically encapsulated	1.54	0.00054	14.0
Anchored	2.26	0.0039	68.8

Table 5
Recycle run results of the heterogenized catalysts

Runs	Conversion (%)		Selectivity (%)	
	A ^a	B ^b	A ^a	B ^b
1	87.8	99.6	80.5	88.2
2	82.9	98.8	80.3	88.1
3	80.0	99.0	80.4	88.2
4	77.0	98.3	80.1	88.0
5	75.2	98.4	79.9	87.7
6	75.7	98.0	79.5	87.8

Conditions: catalyst 0.01 mmol (first run), cyclohexene 2.5 ml, isobutyraldehyde:cyclohexene = 2:1, acetonitrile 60 ml, reaction temperature 60 °C, reaction time 6 h.

^a Physically encapsulated catalyst.

^b Anchored catalyst.

catalyst decreases by only 1.6%, and that the selectivity was kept almost constant after sixth run. However the activity of the physically encapsulated catalyst decreases from 87.8 to 75.7%. It is particularly noted that the conversion reduction is 4.9% from the first to the second run.

For discovering the reasons for the above results we employed ICP to determine the Mn content before and after the catalytic runs. As shown in Table 1, 24.0 and 36.0% of Mn was lost after the second and sixth runs for the physically encapsulated catalyst, respectively. However the Mn content of the anchored one kept almost constant, which indicates no complex leaching took place during the reaction. Thus we can say one reason for the activity deduction of the physically encapsulated catalyst is attributed to the leaching of the complex entrapped in matrix. The slight decrease in the activity of the anchored catalyst may be the pore of the matrix being blocked up by the impurities during the reaction, which prevents reactants from contacting the complex. This can be overcome by ultrasonic treatment [20]. From the results we conclude that an epoxidation catalyst with high activity and good recyclability can be obtained by the combination of chemical binding and sol–gel technique.

4. Conclusions

We synthesized alanine Schiff base manganese(III) complex. The complex was encapsulated in the SiO₂ matrix by direct physical encapsulation and copolymerization of the triethoxysilylpropyl modified complex with TEOS. Both of them were used as the catalyst for the aerobic epoxidation

of cyclohexene and shown better selectivity than the homogeneous complex. The anchored catalyst had the highest activity and selectivity; no complex leaching took place during the catalytic process. It showed the expected advantages of heterogenous catalysts, namely, easy handling and recyclability.

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