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YOUNG SCIENTISTS' SCHOOL

Novel Ways of Mn-Salen Complex Immobilization on Modified Silica Support and Their Catalytic Activity in Cyclooctene Epoxidation[1]

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Abstract—The covalent immobilization of Mn(III)-Salen complexes on an amorphous mesoporous silica support is reported. Both (3-aminopropyl)trimethoxysilane (APTMS) and (3-iodopropyl)trimethoxysilane (IPTMS) were used in a post-synthesis grafting method to prepare organosilane-modified porous materials. Peptide and ester interactions were employed to anchor the Salen complex to the silica framework. The catalytic activity of the immobilized Salen catalyst was studied by epoxidation of cyclooctene. The comparison of the homogeneous and the immobilized catalyst shows that there was no significant loss of catalytic activity for epoxidation by immobilization. In the current study, the effects of reaction temperatures, solvents, and amount of catalyst on the catalytic activity were investigated. The optimal yield of cyclooctene oxide was obtained at 45°C using toluene as the solvent.

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INTRODUCTION

The partial oxidation of alkenes leads to very important intermediates for the production of fine chemicals and polymers. Consequently, several groups work in this field using different catalysts such as heterogeneous supported metal oxide catalysts [1, 2], as well as homogeneous transition metal complex catalysts [3], that can utilize a variety of oxygen sources for the partial oxidation of alkenes.

Manganese(III) complexes of the Schiff base with a N2O2 coordination sphere, which are known in the literature as Salen complexes (Salen-*N*,*N*'-*bis*(salicylidene)-ethylendiamine), have been reported by Larrow and Jacobsen [4] and Katsuki [5] as very efficient catalysts in asymmetric catalytic reactions. The Mn-Salen complexes were also used for the epoxidation of olefins [6, 7]. In view of the problems associated with separating these homogeneous catalysts from the products, significant efforts were undertaken to immobilize the Salen complexes. The catalyst immobilization helps to overcome the problems with catalyst separation, recovery, and recycling. Coordinatively, ion-exchange bound immobilized Salen catalysts have been studied as well [8, 9]. More recently, considerable attention has been given to covalent anchoring of the complexes [10–13].

In the present work, covalent bonding techniques were chosen as the most effective approach to design stable heterogeneous catalysts. The peptide-bound immobilized Mn(III)-Salen complex was also investigated in the catalytic epoxidation reaction.

EXPERIMENTAL

1. Materials

(*R*,*S*)-2,3-Diaminopropionic acid monohydrochloride (99%), triethylamine (99%), 3,4-diaminobenzoic acid (97%), zinc chloride (0.5 M solution in THF), 1-hydroxy-lH-benzotriazole (98%), cyclooctene (95%), *n*-nonane (99%), and extra dry solvents were purchased from Acros Organics. (3-Aminopropyl)trimethoxysilane (98%) and *N*,*N*'-dicyclohexylcarbodiimide (99%) were purchased from Merck. (3-lodopropyl)-trimethoxysilane (95%) and sodium hydroxide were purchased from Fluka. *tert*-Butyl hydroperoxide (6.0 M solution in nonane) was purchased from Aldrich. All chemicals were used as received.

The used amorphous mesoporous silica gel Köstrosorb 1015 was purchased from Chemiewerk Bad Köstritz GmbH. The surface area, average pore volume, and pore size distribution was confirmed by using low temperature nitrogen adsorption-desorption isotherms performed on an ASAP 2010 (Micromeritics). Total surface area and pore volumes were determined using the BET (Brunauer-Emmett-Teller) equation or the single point method. The pore size distribution was obtained from the adsorption branch of the nitrogen isotherms using the density functional theory.

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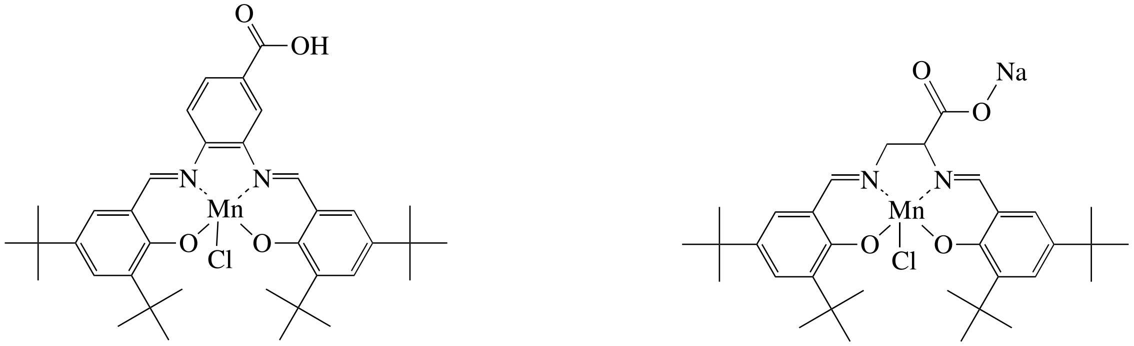
[1] This article was submitted by the authors in English.



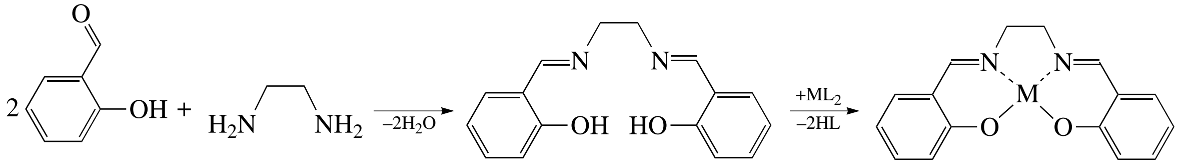
a

N,N'-bis-(3,5-di-*tert*-butylsalicylidene)-1-carboxy-3,4-phenylenediamine manganese (III) chloride

b

Sodium (R, S)-*N,N'-bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminopropionate manganese (III) chloride

Scheme 1. Mn-Salen complex structures applied for immobilization on the silica support.



Scheme 2. The scheme of synthetic procedure of Salen complexes, where M is the metal atom and L is the ligand.

The following substances were synthesized as described in the literature: 3.5-di-*tert*-butylsalicylaldehyde [4], *bis*(tetrahydrofuran) manganese(II) chloride ($MnCl_2(THF)_2$) [14].

2. *Synthesis of Mn(III)-Salen Complexes*

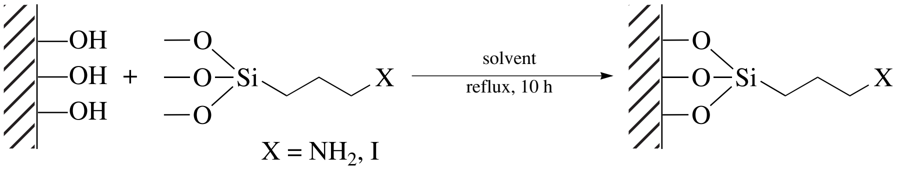
Both Mn-Salen complexes (Scheme 1) were synthesized by a procedure which is shown in Scheme 2 [15]. In the first step of synthesis, the Salen ligands with defined structures were prepared followed by the formation of the manganese(III) complex.

(a) Synthesis of *N,N-bis*(3.5-di-*tert*-butylsalicylidene)-1-carboxy-3.4-phenylene-diamine manganese (III) chloride (Mn-Salen complex a). Salen ligand **a** was prepared as follows: 1.52 g (10.0 mmol) of 3.4-diaminobenzoic acid was suspended in 50 ml of dry tetrahydrofuran (THF). Then, 4.68 g (20.0 mmol) of 3.5-di-*tert*-butylsalicaldehyde dissolved in 40 ml of THF and 20 ml (10.0 mmol) of 0.5 M $ZnCl_2$ solution in THF were added dropwise to the suspension. The resulting mixture was heated under reflux for 45 min, and then the solvent was removed until dryness under reduced pressure. The precipitate was then dissolved in 25 ml of dry methanol; the insoluble residue was filtered and washed three times with 25 ml of methanol. The product was finally recovered as a yellow-green solid (5.43 g, 93% yield) by rotary evaporation.

0.7 g (1.2 mmol) of Salen ligand **a** was completely dissolved in 70 ml of THF followed by the addition of 0.32 g (1.2 mmol) of $MnCl_2(THF)_2$ as a solid within 15 min. The yellow-brown suspension was vigorously stirred at room temperature for 1 h and then boiled for 0.5 h.

The mixture was cooled down to room temperature, and 0.34 ml (2.4 mmol) of triethylamine was slowly added. Air was bubbled through the dark brown solution for 45 min; afterwards, the solvent was evaporated using a rotary evaporator. The residue was dissolved in 20 ml of toluene and stirred at room temperature for 2 h. The mixture was filtered and washed twice with 3 ml of toluene. The resulting black precipitate of the Mn(III)-Salen complex **a** (0.72 g, 89% yield) was collected from the filtrate under reduced pressure.

(b) Synthesis of sodium (*R,S*)-*N,N'-bis*(3.5-di-*tert*-butylsalicylidene)-1.2-diamino-propionate manganese (III) chloride (Mn-Salen complex b). As mentioned previously, the synthesis of Mn-Salen complex **b** was carried out in two stages (Scheme 2). The ligand of complex **b** was prepared by the following way: 1.0 g (7.1 mmol) of (*R*, *S*)-2.3-diaminopropionic acid mono-



Scheme 3. of the silica surface modification.

hydrochloride was suspended in 25 ml of dry methanol followed by the addition of 0.57 g (14.3 mmol) of sodium hydroxide solution in 5 ml of methanol. 3.34 g (14.3 mmol) of 3.5-di-*tert*-butylsalicaldehyde was dissolved in 50 ml of methanol and added dropwise to the stirred solution in a period of 25 min. The yellow reaction mixture was heated under reflux for 20 min. Finally, insoluble impurities were collected by filtration and the solvent was evaporated under vacuum to get the Salen ligand **b** as a yellow precipitate (3.54 g, 89% yield).

In the second stage, the Mn-Salen complex **b** (Scheme 1) was synthesized using ligand **b**. 0.92 g (1.6 mmol) of Salen ligand **b** was dissolved in 50 ml of THF followed by the addition of 0.44 ml (3.1 mmol) of triethylamine. Subsequently, 0.42 g (1.6 mmol) of $MnCl_2(THF)_2$ was slowly (within 15 min) added to the mixture as a solid. The dark brown solution was heated under reflux at the boiling temperature of THF for 1.5 h. After slight cooling, air was blown through the solution for 40 min. Then it was boiled anew under reflux for 2 h followed by evaporation of the solvent. In order to remove the formed triethylammonium chloride, the dark solid residue was dissolved in 25 ml of toluene and filtered using a fine-porous filter. The dark brown solid was recovered from the filtrate by rotary evaporation and dried in vacuum (0.73 g, 72% yield).

3. Preparation of Organo-Functionalized Silica Structures

(3-Aminopropyl)trimethoxysilane and (3-iodopropyl)trimethoxysilane were anchored onto the silica surface via a post-synthesis grafting method to prepare organo-modified mesoporous materials. The procedure of synthesis was similar to that described by Yokoi et al. [16].

In the first step, the amorphous silica gel with a pore volume of 1.1 cm^3/g was heated in vacuum at 70°C for 3 h to remove adsorbed water and organic impurities from the surface. 5.0 g of the prepared silica powder were then suspended in 90 ml of dry toluene followed by the slow addition of 5.0 ml (28 mmol) of APTMS from a syringe. The mixture was vigorously stirred at the boiling point of toluene for 10 h (Scheme 3). The resulting suspension was filtered through a Buchner funnel supplied with a fine-porous filter paper. The collected powder was washed overnight in a Soxhlet extractor using 2-propanol as a solvent and dried in air at 100°C for 5 h.

In the case of iodo-functionalized silica, the procedure was similar to that described above, but the amount of IPTMS used was lower in comparison to the amount of APTMS used; only 2.0 ml (10 mmol) of IPTMS were used, and the reaction took place at room temperature.

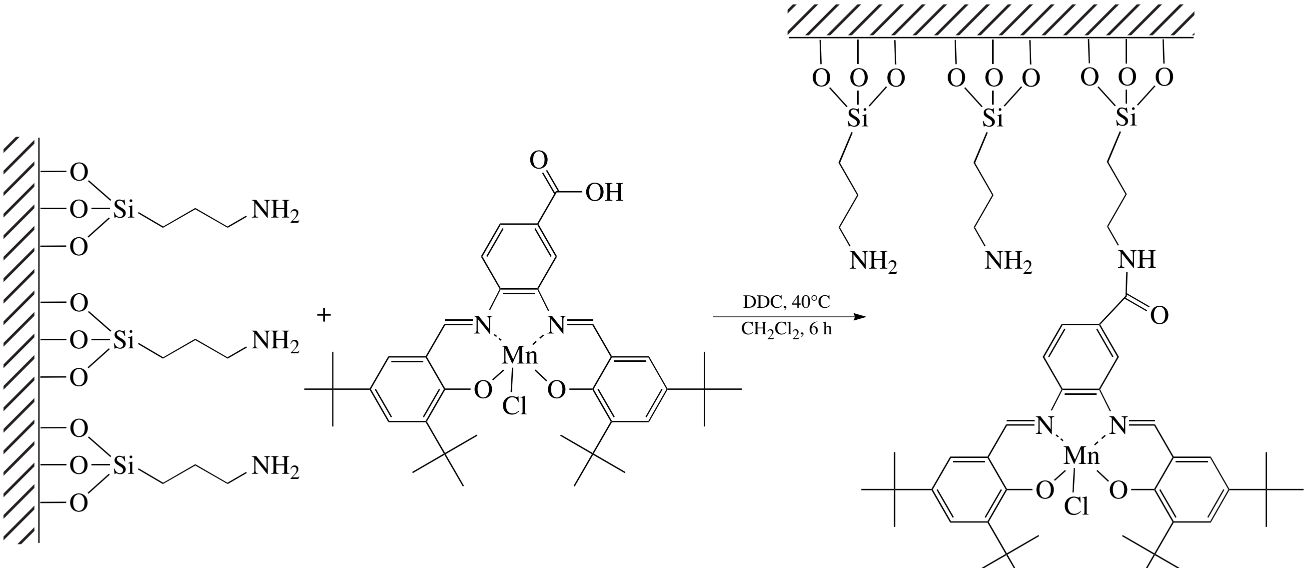
4. Immobilization Procedure

(a) Immobilization of Mn(III)-Salen complex a on an amino-functionalized silica framework via peptide bonding. The synthesis of peptide-bound immobilization was performed using a standard peptide coupling procedure as shown in Scheme 4a. 0.3 g (0.45 mmol) of Mn-Salen complex **a** was dissolved in 6 ml of dry methylene chloride. Afterwards, 0.03 g (0.22 mmol) of 1-hydroxy-1H-benzotriazole was added as a solid. Finally, 0.2 g (0.97 mmol) of *N,N*'-dicyclohexylcarbodiimide solution in 3 ml of CH_2Cl_2 was also added. The mixture was stirred at room temperature for 40 min. Then 1.5 g (2.1 mmol of amino groups) of amino-functionalized silica gel suspended in 2 ml of methylene chloride was slowly added to the prepared mixture. After boiling under reflux for 6 h, a Soxhlet extraction followed with ethanol for 40 h and acetone for 6 h. The product was finally dried in air.

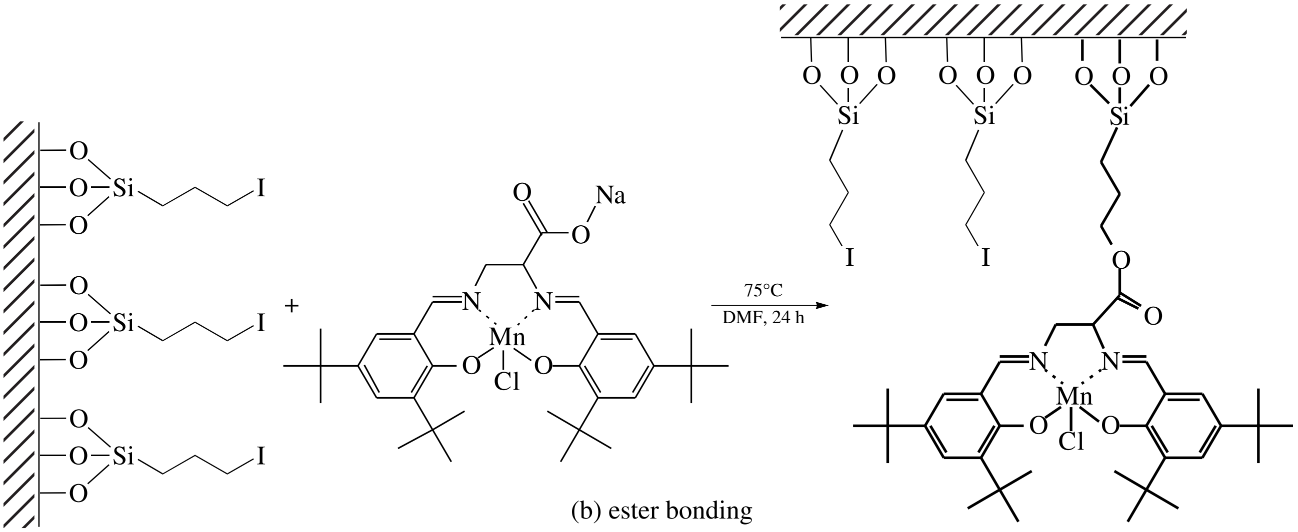
(b) Immobilization of Mn(III)-Salen complex b on an iodo-functionalized silica framework via ester bonding. The ester bound immobilization applied in the present work is illustrated in Fig. 4b and was carried out as follows: 1.5 g (1.35 mmol of iodopropyl groups) of iodo-functionalized silica gel as a solid was slowly added to 0.32 g (0.5 mmol) of Salen complex **b** initially dissolved in 5 ml of dry dimethyl formamide. The dark brown suspension was vigorously stirred at 75°C for 24 h. The product of immobilization was filtered and washed with a Soxhlet extractor using methanol for 18 h. The final product was dried in air.

5. Characterization

(a) Salen complexes. The purity of the obtained Salen ligands was proven by ^{1}H NMR spectra, which



(a) peptide bonding



(b) ester bonding

Scheme 4. The ways of immobilization.

were recorded at 200 MHz with a Varian Gemini-200 NMR spectrometer in a DMSO-d_6 solution. Infrared spectra were recorded on a Genesis FTIR Unicam Analytical System spectrophotometer (ATI Mattson) with KBr pellets. The Mn-Salen complexes were also analyzed by FAB and ESI methods with mass spectroscopy. The melting points of all solid substances were determined by a Boetius micro-melting-point apparatus.

(b) Modified silica gels. The total content of amino groups in amino-functionalized silica gel was determined by CHN elemental analysis, which was performed using a Heraeus CHNO Rapid Analyzer. In the case of iodo-functionalized silica, the amount of iodine was calculated in terms of CH elemental analysis data corresponding to the propyl groups of the organo-modified structure.

Thermogravimetric analyses (TGA) were carried out using STA 409 equipment (Netzsch). A mass spectrometer was used for evolved gas detection. The following conditions were established: heating rate, 10°C min^{-1}; carrier gas, helium; sample mass, 20 mg.

(c) Immobilized catalysts. The catalyst loading on the silica surface was defined by elemental analysis of manganese (using atomic absorption spectroscopy).

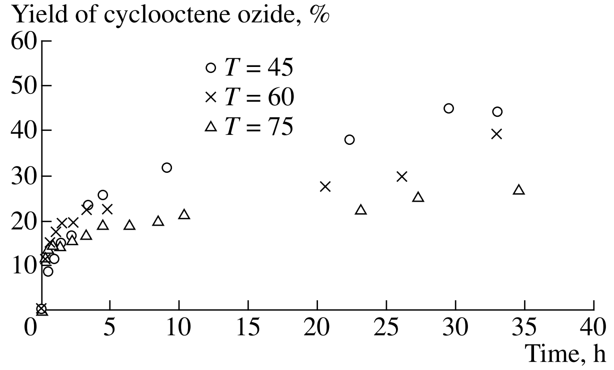


Fig. 1. The temperature effect on the epoxide yield with the homogeneous Mn-Salen complex a as catalyst.

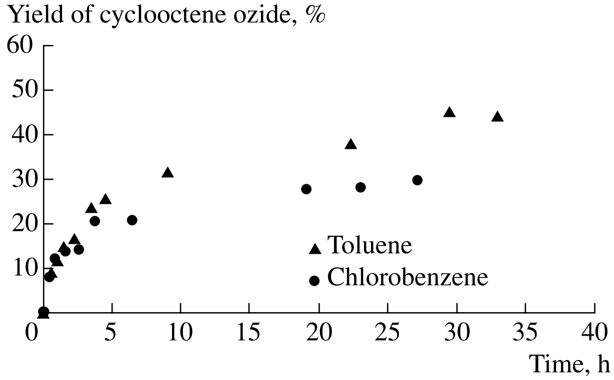


Fig. 2. Effect of solvent on cyclooctene epoxidation.

6. Catalytic Test

The immobilized Mn-Salen complex **a** (Fig. 4a) was explored in the catalytic epoxidation of cyclooctene with *tert*-butyl hydroperoxide (TBHP) as an oxidant. All experiments were carried out in a 10 ml pear-shaped, two-necked flask equipped with a septum, mini-condenser, and magnetic stirrer and placed in an isothermal silicon oil bath where the temperature was controlled by an electronic contact thermometer (ETS D4 fuzzy). The typical reaction mixture was composed of the olefmic substrate (2.7 mmol), TBHP (6.0 mmol), catalyst (0.045 mmol of active centers), and toluene (1 ml) as the solvent. The average time of the reaction was around 40 h. For repeated catalytic experiments, the catalyst was separated using centrifugation followed by decantation, twice washed with toluene and methylene chloride, dried in air, and then used in a new run.

Gas chromatography was used for the identification and the quantification of the reaction products. All analyses were performed with a HP 6890 gas chromatograph equipped with a DB-1 capillary column (60.0 m × 320 m × 0.5 m) and a flame ionization detector. *n*-Nonane was used as an internal standard.

RESULTS AND DISCUSSION

The analysis of the Salen ligands and complexes showed high purity of all synthesized compounds and correlated well with the literature results [15].

The amounts of aminopropyl and iodopropyl coupled to the silica supports—1.4 and 0.9 mmol/g, respectively—were determined by CNH elemental analysis. The organic content in the same samples was also determined by TGA assuming that the weight loss occurring at ca 500°C in the case of amino-functionalized and at ca 350°C for iodo-functionalized silica can be attributed to the combustion of the amino-propyl and iodopropyl groups, respectively. The obtained values are sufficiently close in both methods.

The manganese content of immobilized complexes of type **a** and **b** were as determined by atomic absorption spectroscopy as 1.2 and 0.41 wt %, which means 0.22 and 0.075 mmol/g, respectively. This indicates that, in the case of peptide immobilization, every sixth amino-group of the modified silica gel is used as an anchor for an immobilized complex.

The reaction parameters—namely temperature of the catalytic process, solvent, as well as adduct proportions—were optimized for the highest yield of epoxide. All catalytic experiments were performed with the Mn-Salen complex **a** (Fig. 1) or the peptide bound immobilized catalyst, shown in Fig. 4a. The temperature and the solvent effects were studied at homogeneous conditions of the reaction.

1. Effect of Reaction Temperature on the Epoxidation of Cyclooctene

The epoxidation of cyclooctene was carried out in toluene as a solvent at three temperatures: 45, 60, and 75°C. The results are shown in Fig. 1. There is a visible decrease in epoxide yield with an increase in the temperature. This can be explained by the decrease in efficiency of TBHP with an increase of temperature. It is known that thermal decomposition of organic peroxides is a first order reaction; consequently, an increase in temperature of about 10°C results in a 2- to 3-fold increase in the decomposition rate.

2. Effect of the Solvent

The preliminary solvent selection in the Mn(III)-Salen complex catalyzed epoxidation of cyclooctene was knowledge-based on the complex solubility and volatility of the solvent. Toluene and chlorobenzene have been chosen as acceptable solvents. Acetonitrile was also considered as an appropriate solvent for this catalytic oxidation; however, the Mn-Salen complex is not soluble in it. To study the influence of the solvent on

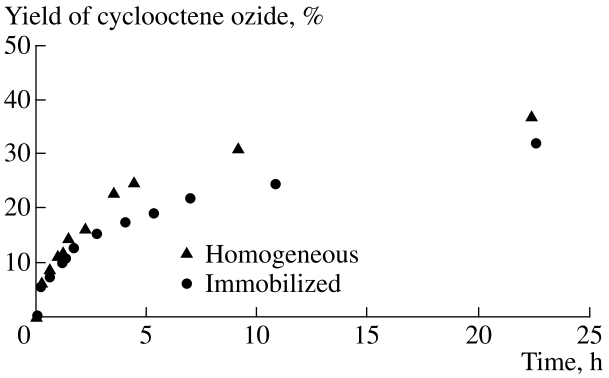


Fig. 3. Comparison of the homogeneous catalyst with the immobilized catalyst at the following conditions: 2.7 mmol of cyclooctene, 6.0 mmol of TBHP, 0.045 mmol (active centers) of catalyst, and 1 ml of toluene as solvent at 45°C.

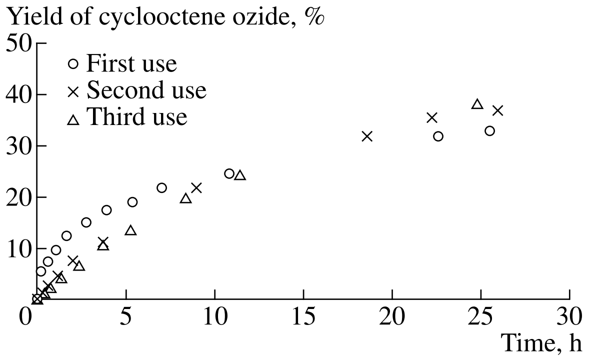


Fig. 4. Repeating of catalytic runs.

catalysis, the solvent was changed while keeping the other conditions identical, i.e., 2.7 mmol of cyclooctene, 6.0 mmol of TBHP, 0.045 mmol (0.03 g) of catalyst **a** and 1 ml of the solvent. The temperature was maintained at 45°C under reflux for 35 h. As can be seen from Fig. 2, there was a small decrease in epoxide yield with chlorobenzene as the solvent.

3. Comparison of the Homogeneous Catalyst with the Immobilized Catalyst

To confirm that the epoxidation reactions are catalyzed in heterogeneous conditions as well, and that a possible small amount of leaching does not contribute to the conversion of olefin, a direct comparison at the same experimental conditions is shown in Fig. 3. The results demonstrate that there is no large difference of catalytic activity in the case of the immobilized catalyst in comparison to the homogeneous complex. The negligible decline of epoxide yield can be explained by diffusion hindrance inside of the porous material.

To prove the influence of diffusion processes in the case of immobilized catalysts, two experiments with different amounts of catalysts were performed. In these catalytic runs, the content of the immobilized Mn-Salen complex **a** was changed from 0.045 mmol to 0.023 mmol while keeping the other conditions constant, i.e., 2.7 mmol of cyclooctene, 6.0 mmol of TBHP in 1 ml of toluene at 45°C. The results show that there was no difference in epoxide yield using different catalyst amounts. This can be due to diffusion obstacles for reacting molecules to reach the active center and for product removal from the silica pores.

4. Reuse of the Spent Catalyst

Experiments were performed in which the immobilized catalyst was used for three consecutive runs in the epoxidation of cyclooctene. The reaction conditions were the same as described before, and the duration of the reaction was 25 h. The results of the epoxidation process with the peptide-bound immobilized complex for three consecutive runs are summarized in Fig. 4. As can be seen, only a small decrease in the epoxide yield was observed when going from the first run to the second and third run. Only in the first 10 h was the reactivity during the second and third run lower than in the first run. This must be due to a difference in activity of the initial state of the catalyst in comparison to the state after the first run. It was observed that the dark brown color of the catalyst during the first 10 h of the first run was turning to a constant yellowish color. This may be the reason why the initial activity was lower in the second and third run.

CONCLUSIONS

Mn-Salen complexes were successfully immobilized in an amorphous mesoporous silica gel support via peptide bonding and ester bonding. The resulting peptide-bound system was tested in the epoxidation of cyclooctene and found to be active. Although the systems were not completely optimized, the catalyst based on the silica surface could be used in at least three consecutive runs. The low total amount of manganese leached cannot account for the very small observed decrease in catalytic activity in successive runs.

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