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Effect of substituents on the Mn(III)Salen catalyzed oxidation of styrene

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Abstract

Manganese(III)complexes of Salen, Br_2Salen and (*tert*-butyl)$_4$Salen ligands and their encapsulated analogues were prepared by the intrazeolite ligand synthesis (template synthesis) method. The oxidation of styrene was studied on the above catalysts using molecular oxygen as oxidant and *tert*-butyl hydroperoxide as initiator. The progress of the reactions was followed both by gas chromatography and by the oxygen consumed. The effect of the substituents on the encapsulation, on the catalytic activity and the effect of the encapsulation on the catalytic activity were studied and discussed.

Keywords: Mn(III)Salen; Ship-in-a-bottle complexes; Intrazeolite synthesis; Aerobic oxidation; Styrene oxidation

1. Introduction

Zeolite encapsulated metal complexes or ship-in-a-bottle complexes comprise a class of biomimetic catalysts sometimes referred to as zeozymes [1–12]. The synthetic faujasite (FAU) type zeolites (Y or X) have been the most widely studied host materials. The FAU structure involves large cavities about 1.2 nm in diameter but the openings to these supercages are only 0.74 nm in diameter. One of the possible strategies for encapsulating metal complexes in such zeolites is the use of the intrazeolite ligand synthesis (or template synthesis) method [1,13]. This procedure involves the in situ assembly of a ligand and the complex that becomes effectively larger than the 0.74 nm windows is then physically entrapped. Homogeneous complexes encapsulated in the pores should be free to move within the confines of the cage such that the solution reactivity should be maintained in a heterogeneous environment. The advantages of site isolation in the pores coupled with the size and shape selectivity of the zeolite support should be reflected in the catalyst activity.

The classic example of such encapsulated compounds is the tetradentate Schiff base H_2Salen molecule (2,2′-[ethane-1,2-diil-bis(nitrilo-methylidyne)]diphenol). The frequently used common name of this molecule is bissalicylidene-ethylene diamine. Manganese complexes of the Salen ligand have been used extensively in low-temperature oxidation reactions. Ratnasamy and co-workers [14] studied the effect of different electron-withdrawing substituents (like chloro, bromo and nitro) on the encapsulation and catalytic activity of Mn(III)Salen catalysts. They synthesized the neat 4,4′-disubstituted molecules (Fig. 1) and encapsulated them by the zeolite synthesis method.

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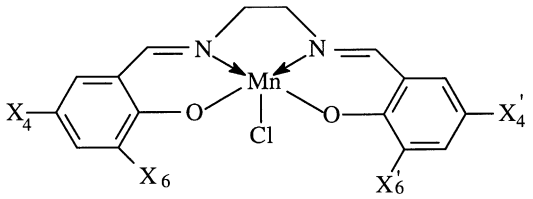

Fig. 1. The structure of the 4,4′,6,6′-substituted-{2,2′-[ethane-1,2-diil-bis(nitrilo-methylidyne)]diphenolato}-manganese(III)-chloride complexes.

These catalysts were used for the oxidation of styrene and it was concluded that the catalytic efficiency of the encapsulated complexes was much higher than that of the neat complexes and the electron-withdrawing substituents enhanced the rate of oxidation.

The goal of the present work is to study the effect of the electron-donating *tert*-butyl group both on the encapsulation of the Salen ligand and the catalytic activity of the catalyst produced. Furthermore, a comparison between the results of the electron-withdrawing and the electron-donating substituents.

2. Experimental

2.1. Materials

2-Hydroxybenzaldehyde (salicylaldehyde), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde, ethylenediamine (99%), manganese (II)acetate tetrahydrate, lithium chloride (99%), acetonitrile (99%), styrene (99%) and NaY zeolite were purchased from Aldrich, while *tert*-butyl hydroperoxide (80% solution in di-*tert*-butyl peroxide) was originated from Merck and used as received. Ethanol (Reanal, 99%) was also used without any additional purification.

2.2. Preparation of neat metal complexes

The neat metal complexes were synthesized by the standard method [14,15]. 2-Hydroxybenzaldehyde or its substituted derivatives (3,5-di-*tert*-butyl-2-hydroxybenzaldehyde or 5-bromo-2-hydroxybenzaldehyde) were reacted with ethylenediamine in ethanol. The solid products were dissolved in hot ethanol and refluxed with manganese(II)acetate tetrahydrate. Lithium chloride was used to produce Mn(III)Salen complexes.

2.3. Preparation of encapsulated complexes

Intrazeolite metal complexes based on the Salen type ligands are prepared normally by the flexible ligand method [1]. However, when the substituents on the aromatic rings of the Salen ligand are bulky *tert*-butyl groups, diffusion of this ligand through the pore openings is hindered. Therefore, this type of encapsulated Mn(III)Salen catalysts are synthesized by the intrazeolite ligand synthesis [13] (or template synthesis [1]) method using NaY zeolite. The unsubstituted and bromo-substituted complexes were prepared in a similar manner for comparative purposes.

2.4. General procedure for the encapsulation

1500 cm^3 of 0.02 M sodium acetate — acetic acid buffer was added to 30 g of NaY. 5.5 g manganese(II)acetate tetrahydrate was dissolved in deionized water and added to the buffered mixture slowly with stirring. Then the solution was stirred for 24 h at room temperature. The slurry was then filtered and the solid was washed with deionized water and dried.

11.4 mmol (1.22 cm^3) 2-hidroxybenzaldehyde (or its substituted analogues) was dissolved in 15 cm^3 ethanol and added to 8 g of Mn-exchanged zeolite. After 4 h stirring 0.38 cm^3 ethylenediamine was added and the mixture was stirred at room temperature for 24 h. The solid was filtered, washed with ethanol and stirred for another 24 h in 100 cm^3 concentrated NaCl solution to remove the uncomplexed manganese ions. The solid material was filtered, washed with deionized water and dried.

2.5. Catalyst characterization

The catalysts were characterized by FT-IR and the metal content was determined by ICP. The FT-IR spectra of the zeolite, the neat complexes and the heterogenized samples were taken, as well. These spectra were recorded in KBr pellets, using Bio-Rad FTS — 65 A spectrophotometer, in the range of 400–4000 cm^{-1}.

To determine the metal content of the heterogenized samples, the samples were dissolved in cc. HNO_3 and HF. The metal content was determined by JOBLIN YVON 24 type ICP-AES instrument, at 257.61 nm. The flow rate of the argon was 12 $dm^3\,min^{-1}$ and the sample dosing was carried out with the speed of 1.5 $cm^3\,min^{-1}$.

2.6. Catalytic reaction

Oxidation reactions were carried out in the liquid phase under one atmosphere of oxygen at room temperature. The apparatus consists of a glass reactor, shaken in a vortex manner and a gas handling system, for monitoring the volume of dioxygen reacted at constant pressure [16,17].

0.1 mmol neat complex (or 0.5 g encapsulated catalyst) was put into the glass reactor and the apparatus was filled with 1 atm of dioxygen. 4 cm^3 acetonitrile and 0.54 cm^3 (4.35 mmol) *tert*-butyl hydroperoxide were added to the catalyst. After a short shaking 0.5 cm^3 (4.35 mmol) styrene was injected into the reactor and the reaction was started with shaking. The product mixture was analyzed at 6, 12, 24 and 48 h by gas chromatography (Hewlett-Packard 5890 Series II), using dichloromethane as internal standard. The products were identified by authentic sample or by Hewlett-Packard 5970 mass selective detector. The amount of styrene, benzaldehyde, phenyloxirane and phenylacetaldehyde was calculated from the chromatograms. In some cases, the reaction was repeated in a higher scale, and an additional product was extracted from the reaction mixture and identified as benzoic acid.

In addition to the gas chromatographic analysis the oxygen consumption was also recorded during the reaction.

3. Results and discussion

3.1. Catalyst characterization

The characteristics of the prepared disubstituted (X_2-Salen) or tetrasubstituted (X_4-Salen) complexes and the encapsulated (Salen-Y) derivatives are shown in Table 1.

The IR spectra of all the neat complexes, the encapsulated samples were recorded. As an example, Fig. 2 shows the IR spectra of the Mn(III)*t*Bu_4Salen complex, the encapsulated catalyst and the NaY zeolite. The IR spectrum of the Mn(III)*t*Bu_4Salen complex show major bands around 1631, 1553, 1535, 1462, 1437, 1411, 1389, 1361, 1306, 1217, 1252, 1200 and 1175 cm^{-1}. Similar frequencies were observed in the case of Mn(III)*t*Bu_4Salen-Y catalyst, indicating the incorporation of the complex. Some differences, however, can be observed between the spectra of the neat and heterogenized complexes, which is even more emphasized on the extended spectrum in the range of 1200–1550 cm^{-1} (Fig. 2).

This difference could be an indication of the encapsulation and might be caused by the distortion of the encapsulated complex.

3.2. Tert-butyl hydroperoxide as initiator

The oxidation of styrene using molecular oxygen was chosen as a model reaction. It was found earlier that styrene could be oxidized with dioxygen alone but the conversion was low. *Tert*-butyl hydroperoxide (2 wt.% of styrene) as initiator, however, can increase the oxidation efficiency of the molecular oxygen [14]. At the same time in the absence of dioxygen (under an argon atmosphere) the Mn(III)Salen complexes did not show substantial catalytic activity

Table 1
Characteristics of the prepared neat and encapsulated catalysts

Catalysts	X_4 (Fig. 1)	X_6 (Fig. 1)	Mn(III) complex (mmol/gram catalyst)
Mn(III)Salen	H	H	–
Mn(III)Salen-Y	H	H	0.027
Mn(III)*t*Bu_4Salen	*t*Bu	*t*Bu	–
Mn(III)*t*Bu_4Salen-Y	*t*Bu	*t*Bu	0.115
Mn(III)Br_2Salen	Br	H	–
Mn(III)Br_2Salen-Y	Br	H	0.040

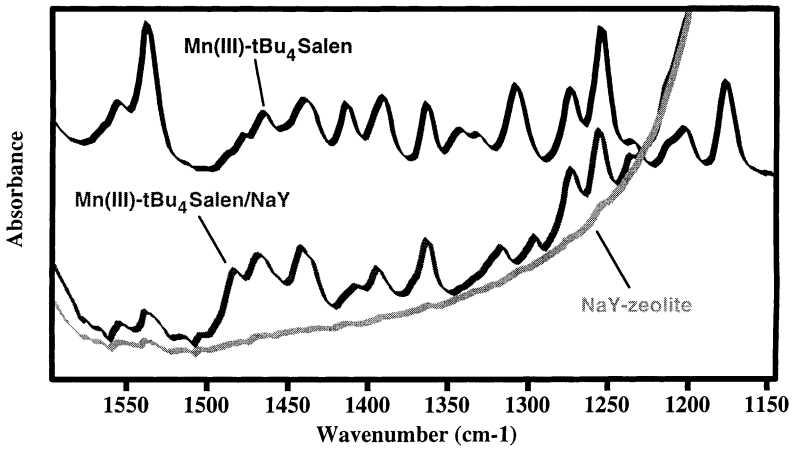

Fig. 2. FTIR spectra of NaY zeolite, Mn(III)*t*Bu$_4$Salen and Mn(III)*t*Bu$_4$Salen-Y catalysts.

[18]. It means that the above effect is a synergetic one.

In the oxidation reaction acetonitrile was used as solvent, because this is the best solvent for the Mn(III)Salen type complexes. However, the complete dissolution of the complexes is difficult, especially in the case of the Mn(III)Br$_2$Salen complex. We found that adding a certain amount of *tert*-butyl hydroperoxide to the reaction mixture before the reaction, makes easier to dissolve the complex. Since the catalyst and the *tert*-butyl hydroperoxide form an adduct which is the active intermediate in the oxidation reaction [18]. This adduct has a much better solubility than the original compound, a sufficient amount of *tert*-butyl hydroperoxide may dissolve the whole amount of complex. This is a crucial point, because if we want to compare the specific catalytic activity of the homogeneous complexes to the encapsulated ones, the neat complexes must be completely dissolved. Since in the homogeneous circumstances only those part of the neat complex is active, which is dissolved.

We have found that 4 mmol *tert*-butyl hydroperoxide seems to be enough to dissolve 0.1 mmol neat complex used in the reaction. Since the relatively high amount of *tert*-butyl hydroperoxide, the reaction progress was followed both by gas chromatography and by the oxygen consumption. We also wanted to check, whether the molecular oxygen is the real oxidant or not.

3.3. Oxidation with neat complexes

The major product of the oxidation of styrene is benzaldehyde together with phenyloxirane (styrene oxide). Fig. 3 shows the conversion values of styrene and Table 2 shows the selectivity data based on the gas chromatographic analysis.

Fig. 3 and Table 2 show that, all of the catalysts were active in the oxidation of styrene. The shape of the curves based on the dioxygen consumption data

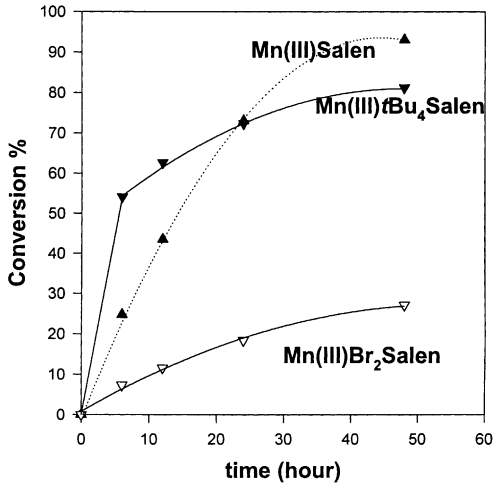

Fig. 3. Percent styrene conversion values on different Mn(III)Salen type catalysts.

Table 2
Product selectivities (%) in oxidation of styrene on different Mn(III)Salen type catalysts (substrate to catalyst ratio = 43.5)

Catalysts	Products	6 h	12 h	24 h	48 h
Mn(III)Salen	Benzaldehyde	35.5	26.2	18.3	16.0
	Phenyloxirane	5.2	5.3	4.9	6.0
	Benzoic acid	59.3	68.5	76.6	78.0
Mn(III)*t*Bu$_4$Salen	Benzaldehyde	35.0	31.4	26.4	22.6
	Phenyloxirane	7.9	8.3	7.6	7.1
	Benzoic acid	57.1	60.2	66.0	70.3
Mn(III)Br$_2$Salen	Benzaldehyde	60.3	67.3	70.1	76.5
	Phenyloxirane	5.5	4.3	3.8	3.8
	Benzoic acid	34.2	28.4	26.1	19.6

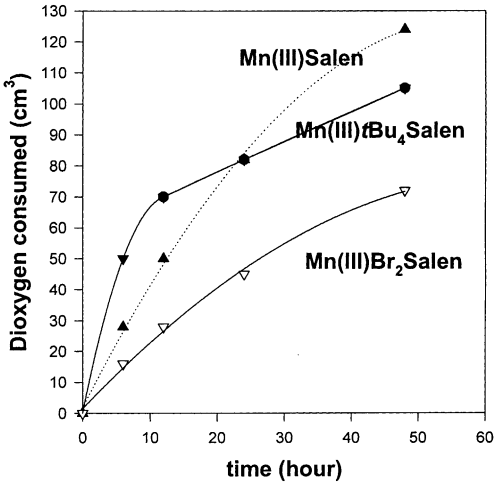

Fig. 4. Oxygen consumption during the oxidation of styrene on different Mn(III)Salen catalysts.

(Fig. 4) were very similar to the gas chromatographic curves in Fig. 3, supporting the assumption [18] that, dioxygen is the real oxidant in this reaction.

The initial specific rate values were calculated from the experimental data (Table 3).

The electron-donating *tert*-butyl groups increased the initial rate significantly. With a small amount of *tert*-butyl hydroperoxide (2 wt.% of styrene) the bromo-substituent increased the catalytic activity, too [14]. In this work, however, large amount of *tert*-butyl hydroperoxide was used and the bromo-substituent had a reverse effect. Namely, the substituted derivative had a lower initial rate than the none substituted one. The highest initial rate was observed in the case of the *tert*-butyl substituents, but the deactivation of this catalyst was also found. After 24 h the rate on this catalyst was lower than the rate on Mn(III)Salen. It was also observed, that the Mn(III)*t*Bu$_4$Salen catalyst decomposed the *tert*-butyl hydroperoxide molecules, meanwhile dioxygen evolved. The observed deactivation may be attributed to this decomposition.

3.4. The effect of substituents on the encapsulation

In this work, the intrazeolite ligand synthesis method was used for the preparation of the encapsulated catalysts. This method produced the lowest complex concentration in the case of Mn(III)Salen-Y catalyst (Table 1). Both of the two other derivatives had a higher complex concentration in the zeolite. Since the highest complex concentration was observed in the case of Mn(III)*t*Bu$_4$Salen-Y, we believe that the increase in the size of the complex, to be encapsulated increases its encapsulation efficiency. This fact seems to be independent from the electron-withdrawing or electron-donating nature of the substituents. It seems, that the increase in size of the complex enhances its physical entrapping in the zeolite supercage.

3.5. Oxidation with encapsulated complexes

The encapsulated analogues of the three homogeneous Mn(III)Salen complexes were also used in the oxidation of styrene. According to the literature (e.g.

Table 3
Initial specific rate values (mol styrene converted/mol Mn(III)complex) at different Mn(III)Salen catalysts and the ratio of encapsulated rate values to homogeneous ones

Catalysts	Initial rates	Catalysts	Initial rates	Ratio
Mn(III)Salen	1.8	Mn(III)Salen-Y	7.3	4.0
Mn(III)*t*Bu$_4$Salen	4.0	Mn(III)*t*Bu$_4$Salen-Y	3.9	0.98
Mn(III)Br$_2$Salen	0.6	Mn(III)Br$_2$Salen-Y	5.0	8.3

[14]) encapsulation generally increases the specific activity of the catalysts. The amount of the complex in the encapsulated catalysts used in the catalytic reactions is usually much lower (in some cases by two magnitudes) than in the homogeneous reaction. For the better comparison, in this work the amount of complexes were almost the same in the homogeneous and in the heterogeneous case.

Using encapsulated catalysts the product distribution was similar to the homogeneous reactions, except phenylacetaldehyde was observed on the heterogenized catalysts. It is probable, that this product is formed via ring opening of phenyloxirane on the acidic sites of the zeolite. It is well known, that benzyl oxiranes are very sensitive to the presence of even a very small amount of acidic sites.

Fig. 5 shows the conversion values of styrene and Table 4 shows the selectivity data based on the gas chromatographic analysis. The initial respective rate values were also calculated (Table 3).

In this case the Mn(III)Salen-Y was the most active catalyst, while both substituents decreased the respective reaction rate in the case of encapsulated catalysts.

3.6. The effect of encapsulation on the catalytic activity

The encapsulation increased the respective catalytic activity in the case of the Mn(III)Salen-Y and Mn(III)Br_2Salen-Y catalysts, while the neat and encapsulated Mn(III)*t*Bu_4Salen complexes had almost the same specific catalytic activity (Table 3).

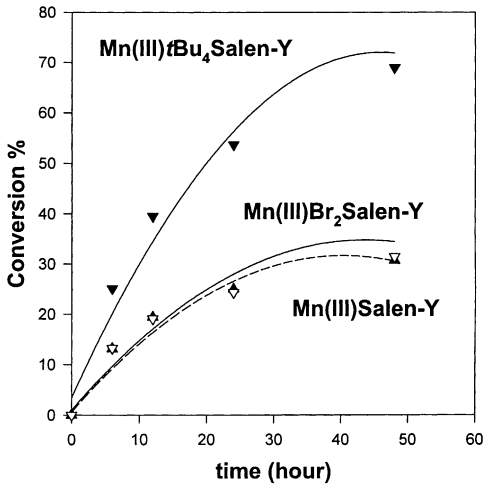

Fig. 5. Percent styrene conversion values on different Mn(III)Salen-Y catalysts.

The encapsulation increased the catalytic activity according to the following trend: Mn(III)Br_2Salen > Mn(III)Salen > Mn(III)*t*Bu_4Salen. This trend is opposite to the solubility trend: Mn(III)Br_2Salen < Mn(III)Salen < Mn(III)*t*Bu_4Salen. The rate increasing effect of the encapsulation may be attributed to the fact that the neat complexes are not completely dispersed molecularly in the reaction mixture, while the encapsulated ones are molecularly dispersed in the zeolite. The Mn(III)Br_2Salen has the lowest solubility in the reaction mixture, consequently, this complex produced the highest rate increase by encapsulation. In the case of the Mn(III)*t*Bu_4Salen, however, which

Table 4
Product selectivities (%) in oxidation of styrene on different encapsulated Mn(III)Salen type catalysts

Catalysts	Products	6 h	12 h	24 h	48 h
Mn(III)Salen-Y (substrate to catalyst ratio = 322)	Benzaldehyde	29.7	30.4	30.8	30.9
	Phenyloxirane	0.8	1.0	1.2	1.3
	Phenylacetaldehyde	1.6	2.6	3.6	5.8
	Benzoic acid	67.9	66.0	64.8	62.2
Mn(III)*t*Bu_4Salen-Y (substrate to catalyst ratio = 75)	Benzaldehyde	28.7	34.2	38.2	35.2
	Phenyloxirane	1.2	3.5	4.6	5.4
	Phenylacetaldehyde	6.0	19.0	21.6	16.5
	Benzoic acid	64.1	43.5	35.6	42.8
Mn(III)Br_2Salen-Y (substrate to catalyst ratio = 217)	Benzaldehyde	24.2	30.4	42.9	51.6
	Phenyloxirane	0.0	0.5	1.2	1.6
	Phenylacetaldehyde	0.8	1.0	1.6	2.6
	Benzoic acid	75.0	68.1	54.3	44.2

has the best solubility, the catalytic activity did not increased by the encapsulation at all.

3.7. The effect of encapsulation on the catalyst stability

We have also observed an interesting difference between the neat and the encapsulated catalysts, concerning their stability. The initial catalytic activity of the Mn(III)*t*Bu$_4$Salen catalyst is the highest, but its activity decreases during the reaction and after 24 h the rate is lower than on Mn(III)Salen. Similar effect, however, was not observed in the case of the encapsulated catalyst. We assumed earlier, that this deactivation may be attributed to the decomposition of the *tert*-butyl hydroperoxide. In the case of the encapsulated complexes this decomposition cannot affect the solubility of the complexes, consequently has no effect on the reaction rate.

3.8. The effect of encapsulation on the selectivity

The Mn(III)*t*Bu$_4$Salen was the most active complex for the oxidation of styrene and, of course, this catalyst produced the highest amount of phenyloxirane, too. On the Mn(III)*t*Bu$_4$Salen-Y catalyst large amount of phenylacetaldehyde was also observed. It is very likely that the phenylacetaldeyde is produced by the acidic cleavage of phenyloxirane. Therefore, the sum of the phenylacetaldehyde and phenyloxirane was presented on Fig. 6 in the case of Mn(III)*t*Bu$_4$Salen-Y catalyst. As can be seen the encapsulation made this catalyst much more active for the epoxidation.

3.9. The effect of substituents on the catalytic activity

We found that in the case of the neat complexes the activity trend agrees well with the solubility trend. So, we believe that the substituents influence mainly the solubility, consequently the catalytic activity.

In the case of encapsulated catalysts the activity trend: Mn(III)Salen > Mn(III)Br$_2$Salen > Mn(III)*t*Bu$_4$Salen is opposite to the concentration of the complexes in the zeolite. Comparing the heterogenized and the homogeneous catalysts, the rate increase (four to seven-fold) is much smaller than it was observed by Ratnasamy and co-workers (20–35-fold)

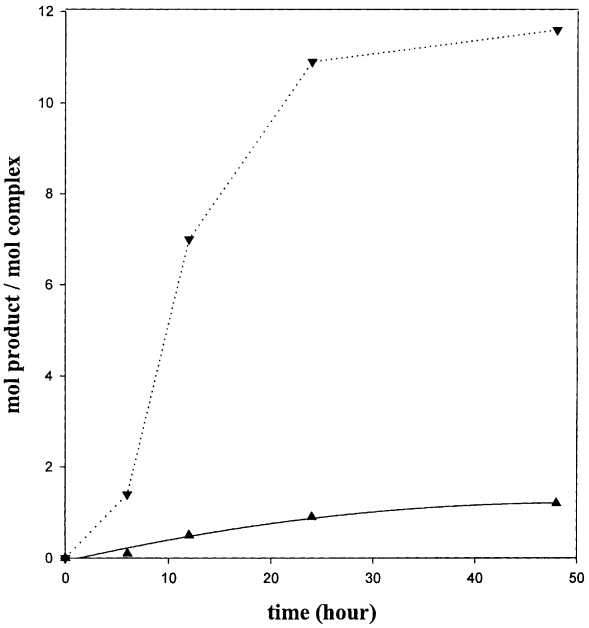

Fig. 6. Production of phenyloxirane on Mn(III)*t*Bu$_4$Salen (▲) or phenyloxirane + phenylacetaldehyde on Mn(III)*t*Bu$_4$Salen-Y (▼) catalysts.

[14]. Since the amount of catalysts, used in the reaction was almost the same in both works, we believe that their method produced lower complex concentration in the zeolite, consequently higher specific rate.

Our experimental data show that the electron-withdrawing or electron-donating ability of the substituents can affect the solubility of the neat complexes; consequently, its catalytic activity. However, in the case of the encapsulated catalysts the solubility difference does not have any effect on the activity of the catalysts. Ratnasamy and co-workers [14] have also observed a significant rate increase in the case of the bromo-substituted derivative in the homogeneous condition, while in the case of the encapsulated catalyst only a small effect was observed.

4. Conclusions

1. Both the neat and encapsulated Mn(III)Salen complexes were active in the oxidation of styrene

at room temperature using 1 atm of molecular oxygen, as oxidant and *tert*-butyl hydroperoxide, as initiator.

2. Dioxygen is the real oxidant in this reaction, in spite of the relatively large amount of *tert*-butyl hydroperoxide used.
3. The higher amount of *tert*-butyl hydroperoxide (4–1 mmol complex) can promote the reaction by increasing the solubility of the complexes.
4. In the case of the neat complexes, the activity trend agrees well with the solubility trend: Mn(III)Br_2Salen < Mn(III)Salen < Mn(III)*t*Bu_4Salen, while for the encapsulated catalysts the trend of the specific activity: Mn(III)Salen-Y > Mn(III)Br_2Salen-Y > Mn(III)*t*Bu_4Salen-Y is just opposite to the concentration of the complexes in the zeolites.
5. In the case of the Mn(III)Salen-Y and Mn(III)Br_2 Salen-Y catalysts the encapsulation increased the catalytic activity, while the neat and encapsulated Mn(III)*t*Bu_4Salen complexes had almost the same reactivity.
6. It is very likely that the different solubility is responsible for the different activity in the homogeneous condition. The encapsulated molecules, however, are molecularly dispersed, and the solubility differences have no effect on the catalytic activity.
7. Using the intrazeolite ligand synthesis (or template synthesis) method, the increase in the size of the complexes seems to enhance their physical entrapping in the zeolite. This feature is independent of the electron-withdrawing or electron-donating nature of the substituents.
8. The encapsulation produced more stable catalysts, especially in the case of Mn(III)*t*Bu_4Salen catalyst.

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