

(Salen)nickel-Catalysed Epoxidations in the Homogeneous and Heterogeneous Phase: The Implications of Oxygen on the Efficiency and Product Selectivity

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The catalytic activity of several nickel(II) complexes with salen-type ligands and their zeolite-immobilised analogues is assessed in the epoxidation of *trans*- β -methylstyrene by NaOCl, in the absence and in the presence of oxygen. The complexes were immobilised in zeolites X and Y using the "ship-in-a-bottle" procedure, and the resulting materials were characterised by chemical analysis, XPS and IR, and UV/Vis diffuse reflectance spectroscopy. The loading and the distribution of the complexes in the materials were found to be dependent on the ligand. All (salen)nickel complexes proved to be active in the homogeneous and heterogeneous epoxidation of *trans*- β -methylstyrene by NaOCl. The im-

mobilised complexes gave lower conversions and their catalytic activity is dependent on the loading and distribution of the complexes within the zeolites. In both homogeneous and heterogeneous systems, the alkene conversion is influenced by oxygen. Removing oxygen from the reaction media results in lower alkene conversion but higher epoxide selectivity. Based on these results, two competitive mechanisms are proposed for the epoxidation reaction, one implying the formation of free radicals and other involving the binding of the substrate to a (oxo)metal intermediate.

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Introduction

The use of transition metal complexes as catalysts for the epoxidation of alkenes has been a subject of interest in the past few decades due to the increasing use of epoxides in agro- and pharmacological chemistry.^[1] A large number of publications concern the use of the (salen)Mn complexes developed by Katsuki and Jacobsen as highly enantioselective catalysts in the epoxidation of alkenes.^[2–4] In these studies, oxidants such as *tert*-butyl hydroperoxide and iodosylbenzene are often employed, although lately the use of environmentally more friendly oxidants such as H₂O₂ and NaOCl has been pursued.

Although (salen)nickel(II) complexes have not been as widely investigated as their manganese analogues, earlier studies by Burrows and co-workers, and later by Kureshy, proved that nickel complexes with cyclam and salen ligands are also active catalysts in the epoxidation of alkenes.^[5–10]

The immobilisation of transition metal complexes in solid supports has intrinsic practical advantages, namely the heterogenised catalysts are easy to handle and can be re-

used.^[11,12] Transition metal complexes can be immobilised in several supports such as zeolites,^[13] activated carbon^[14] and pillared clays.^[15] Recently, we demonstrated that (salen)-manganese complexes immobilised in carbon and pillared clays can be used as heterogeneous catalysts in epoxidation reactions without significant loss in their catalytic activity upon re-use.^[16–18]

The immobilisation and employment of (salen)nickel complexes in heterogeneous catalysis has not been extensively explored. Some examples include the use of (salen)-Ni-type complexes in faujasites for the oxidation of phenol with H₂O₂^[19] and for the epoxidation of cyclohexene and 1-hexene by NaOCl.^[20,21] A more recent study concerned the use of [Ni(salen)] immobilised in several solid supports as a catalyst for hydrogenation reactions.^[22]

This paper exploits the use of (salen)Ni^{II} complexes as homogeneous catalysts and, after immobilisation in zeolites X and Y, as heterogeneous catalysts in the epoxidation of *trans*- β -methylstyrene by NaOCl. Zeolites X and Y have a crystalline faujasite-type structure composed of small pores (diameter 7 Å), which access internal cavities with a diameter of 13 Å. This topology originates two special properties: (i) zeolites can act as molecular sieves, and (ii) they can be hosts by accommodating and restricting molecules inside the cavities. When considering the potential use of zeolites as supports for catalysts, the above characteristics can result in very important features such as reactant/product size- and shape selectivity and the possibility to host metal complexes that have proved to be good catalysts in solution. Nevertheless, it is noteworthy that the catalyst performance

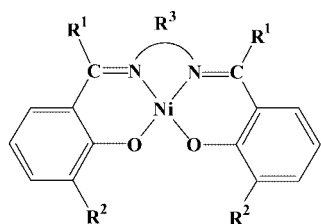
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can be affected by the immobilisation in a solid material with its own physical and chemical properties.

Four different (salen)Ni^{II} complexes (Scheme 1) were encapsulated in both zeolites X and Y using the “ship-in-a-bottle” procedure^[23] accomplished by the “flexible ligand” approach. This two-step synthesis consists of (i) the introduction of Ni^{II} cations by ion exchange and (ii) solvent-free diffusion of the ligands, followed by complexation with the nickel ions. The four (salen)nickel(II) complexes meet the requirements needed for this method of immobilisation because their ligands have a suitable size to diffuse through the pores and reach the cavities containing the metal ions.



	R ¹	R ²	R ³
1 [Ni(salen)]	H	H	CH ₂ CH ₂
2 [Ni(salhd)]	H	H	cyclo-C ₆ H ₁₀ (<i>cis/trans</i> mixture)
3 [Ni(α,α' -Me ₂ salen)]	CH ₃	H	CH ₂ CH ₂
4 [Ni(3-MeOsalen)]	H	CH ₃ O	CH ₂ CH ₂

Scheme 1. Structure of (salen)nickel(II) complexes.

The catalytic activity of the materials was then tested in the epoxidation of *trans*- β -methylstyrene by NaOCl and compared with the results obtained for the complexes in the homogeneous phase. In order to understand the effect of molecular oxygen, a possible co-oxidant, all the reactions were performed in the presence and in the absence of oxygen. These experiments have enabled us to obtain insights into the mechanism of the alkene epoxidation by nickel complexes.

Results and Discussion

Materials Characterisation

The ship-in-a-bottle synthesis resulted in an efficient loading of the nickel complexes inside the zeolites. The loading of the complexes and their distribution within the material was deduced from the nickel content determined by bulk chemical analysis and from XPS. Table 1 presents the nickel content of the materials (wt.-% Ni) obtained by chemical bulk analysis and the Ni/Si ratio obtained by chemical analysis and by XPS.

Table 1. Nickel content (% weight) obtained by chemical analysis (CA) and Ni/Si ratios obtained by chemical analysis (CA) and XPS for the immobilised (salen)nickel(II) complexes.

Catalyst	wt.-% Ni (CA)	Ni/Si	
		CA	XPS
[Ni(salen)]@X	1.0	0.040	0.176
[Ni(salhd)]@X	1.9	0.053	0.142
[Ni(α,α' -Me ₂ salen)]@X	1.0	0.033	0.196
[Ni(3-MeOsalen)]@X	1.8	0.050	0.161
[Ni(salen)]@Y	1.0	0.019	0.101
[Ni(salhd)]@Y	1.3	0.055	0.074
[Ni(α,α' -Me ₂ salen)]@Y	0.4	0.011	0.117
[Ni(3-MeOsalen)]@Y	1.5	0.031	0.074

The results in Table 1 show that the amount of complex and its distribution within the solids differs with the size of the complex and with the zeolite type. Loadings between 0.4 and 1.8 wt.-% Ni were obtained, but generally zeolite X presents a slightly higher complex content than zeolite Y. This is explained by the higher number of exchangeable cations present in the parent NaX (Na/Si = 0.7) when compared with NaY (Na/Si = 0.4), which results in a higher number of Ni^{II} cations in the cavities and, consequently, a higher complex loading.

In both zeolites X and Y, the complexes [Ni(3-MeOsalen)] and [Ni(salhd)] have a higher content inside the zeolites. Also, the distribution of the complexes depends on the ligand type. All the complexes show a higher Ni/Si ratio by XPS than by chemical analysis, pointing to a preferential location of the complexes in the outer layers. This difference is more significant for [Ni(salen)] and [Ni(α,α' -Me₂salen)], suggesting that these complexes occupy more the surface layers while [Ni(3-MeOsalen)] and [Ni(salhd)] are more uniformly distributed.

The preferential location in the outer layers could be due to diffusion of the complexes out of the inner cavities, probably during the extraction step.

The IR spectra of the solids were recorded and compared with the IR spectra of the corresponding free complexes. Figures 1a and 1b show the IR spectra of [Ni(salen)]@X and [Ni(salen)]@Y, respectively, in the region 2000–1000 cm⁻¹. For comparison, the spectra of the parent materials, NiX, NiY, and of [Ni(salen)] are also included. All the materials present intense bands in this region due to zeolite lattice vibrations (1200–1000 cm⁻¹) and a large band centred at 1620 cm⁻¹ attributed to adsorbed water.^[24]

The characteristic bands of the complex are observed in the region between 1600 and 1200 cm⁻¹, where the zeolites do not absorb, and represent the $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{C})$, $\nu(\text{C}-\text{C})$ and $\nu(\text{C}-\text{O})$ vibrations. The frequencies of these vibrations are practically coincident with those of the complexes, thus providing evidence for their presence inside the zeolites without significant interaction with the matrixes.

The encapsulation of the complexes was also confirmed by UV/Vis diffuse reflectance. Figures 2a and b display typical UV/Vis diffuse reflectance spectra of [Ni(salen)]@X and [Ni(salen)]@Y, respectively. The spectra of the corresponding original materials, NiX and NiY, and of [Ni(salen)] are included for comparison.

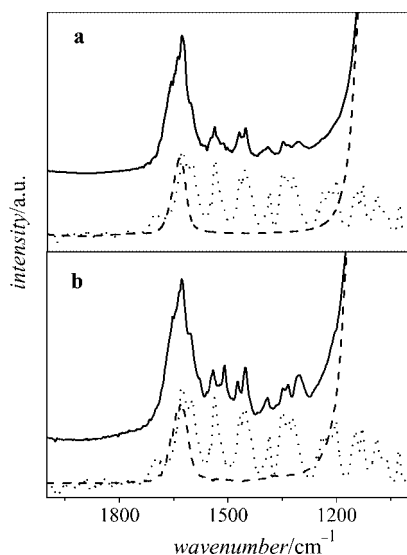


Figure 1. a) IR spectra of [Ni(salen)]@X (solid line), [Ni(salen)] free complex (dotted line) and the parent NiX (dashed line), and b) IR spectra of [Ni(salen)]@Y (solid line), [Ni(salen)] free complex (dotted line) and the parent NiY (dashed line).

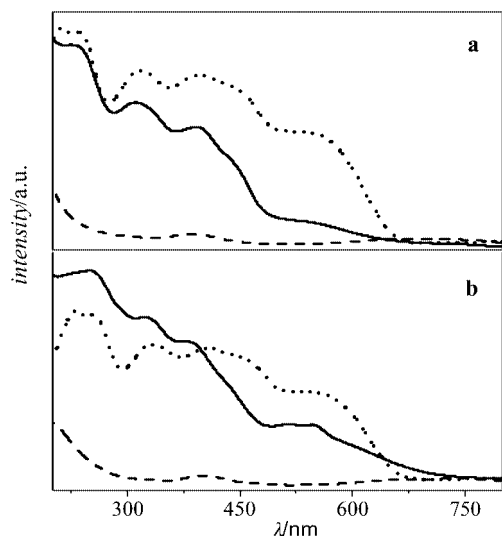


Figure 2. a) UV/Vis solid-state diffuse reflectance spectra of [Ni(salen)]@X (solid line), [Ni(salen)] (dotted line) and NiX (dashed line), and b) UV/Vis solid-state diffuse reflectance spectra of [Ni(salen)]@Y (solid line), [Ni(salen)] (dotted line) and NiY (dashed line).

All the materials exhibit bands in the range $\lambda = 300\text{--}700\text{ nm}$. The bands with $\lambda_{\text{max}} < 450\text{ nm}$ were attributed to charge-transfer bands. Characteristic d-d bands appear at 510–560 nm in the spectra of the free complexes as well as in the spectra of the zeolite-immobilised complexes. However, the materials show slight shifts of the transition bands in relation to the free complexes, thus suggesting some degree of distortion around the metal centre, probably induced by the immobilisation.

Homogeneous Catalysis

The catalytic activity of the four (salen)nickel(II) complexes was first studied in the homogeneous phase (sub-

strate/catalyst ratio = 0.025:1, in dichloromethane) with NaOCl as oxidant. The experiments were run in the presence and in the absence of oxygen. Figure 3 shows the alkene conversion as a function of the reaction time for the epoxidation of *trans*- β -methylstyrene catalysed by [Ni(salen)], [Ni(salhd)], [Ni(α,α' -Me₂salen)] and [Ni(3-MeOsalen)] in the presence of oxygen. It is clear from this figure that all complexes are active catalysts in the reaction. The conversion follows a sigmoid curve with an induction period of about 1 h, and reaches maximum conversion after 10 h. The presence of an induction period suggests that the oxidant efficiency is limited.^[25]

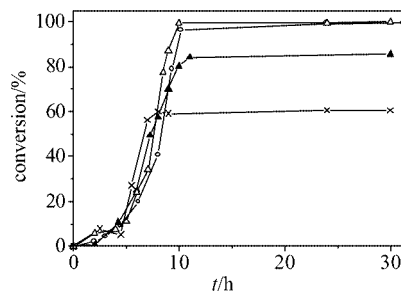


Figure 3. Conversion vs. time plot of the epoxidation of *trans*- β -methylstyrene with NaOCl catalysed by [Ni(salen)] (Δ), [Ni(salhd)] ($\circ$), [Ni(α,α' -Me₂salen)] ($\blacktriangle$) and [Ni(3-MeOsalen)] ($\times$) in the presence of oxygen.

Figure 4 shows the alkene conversion as a function of the reaction time obtained in the epoxidation of *trans*- β -methylstyrene catalysed by [Ni(salen)], [Ni(salhd)], [Ni(α,α' -Me₂salen)] and [Ni(3-MeOsalen)], in the absence of oxygen. All the complexes are also active in the absence of oxygen and the evolution with time pursues a similar pattern as observed in the presence of oxygen: a sigmoidal curve with an induction period, although the reaction is slower and the time needed to reach the maximum conversion is about 20 h. The induction period is higher in this case, and dependent on the complex. Table 2 summarises the results obtained after 24 h for the reactions catalysed by the nickel(II) complexes in the homogeneous phase under aerobic or anaerobic conditions.

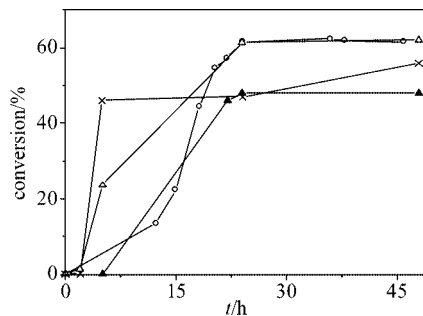


Figure 4. Conversion vs. time plot of the epoxidation of *trans*- β -methylstyrene with NaOCl catalysed by [Ni(salen)] (Δ), [Ni(salhd)] ($\circ$), [Ni(α,α' -Me₂salen)] ($\blacktriangle$) and [Ni(3-MeOsalen)] ($\times$) in the absence of oxygen.

Alkene conversions of between 61 and 100% were obtained in the presence of oxygen and between 47 and 65%

Table 2. Epoxidation reactions with the free complexes in the presence and absence of oxygen.^[a]

Catalyst	O ₂ ^[b]	Conv. [%] ^[c]	Selectivity [%] (Yield [%])		
			Epoxide ^[d]	Benzaldehyde	Others
[Ni(salen)]	present	100	54 (54)	9 (1)	37 (4)
[Ni(salhd)]	present	99	54 (54)	11 (11)	35 (3)
[Ni(α,α' -Me ₂ salen)]	present	84	58 (49)	11 (9)	31 (26)
[Ni(3-MeOsalen)]	present	61	52 (32)	12 (7)	36 (22)
[Ni(salen)]	absent	62	60 (37)	8 (5)	32 (20)
[Ni(salhd)]	absent	65	65 (42)	15 (10)	20 (13)
[Ni(α,α' -Me ₂ salen)]	absent	48	69 (33)	9 (4)	22 (11)
[Ni(3-MeOsalen)]	absent	47	47 (22)	9 (4)	44 (21)

[a] Solvent: CH₂Cl₂; alkene/catalyst ratio = 1.0:0.025; results after 24 h. [b] Oxygen is present as in normal atmosphere (1 atm). For the conditions in the absence of oxygen, see Exp. Sect. [c] Conversion (as disappearance of alkene) determined by GC using *n*-decane as internal standard. [d] Obtained as 100% *trans*-epoxide.

in its absence; epoxide was the major product but benzaldehyde and other products were also obtained.^[26]

In the presence of oxygen, the reactions catalysed by [Ni(salen)] and [Ni(salhd)] show the highest conversion, reaching almost 100%. The introduction of two methyl groups at the α -imine carbon atom in [Ni(α,α' -Me₂salen)] decreases the conversion but does not affect the epoxide selectivity. The effect of an electron-donor group in the third position of the aldehyde fragment is more significant: the methoxy group in [Ni(3-MeOsalen)] decreases the conversion significantly (61%), although the epoxide selectivity is not affected. No significant changes were observed when the aliphatic imine bridge was substituted by a cyclohexyl bridge, as in [Ni(salhd)]. In general, the selectivity of the products does not seem to be dependent on the ligand: [Ni(α,α' -Me₂salen)] shows the highest value for the epoxide selectivity (58%) whereas [Ni(3-MeOsalen)] has the lowest value (52%).

For the reactions in the absence of oxygen, the alkene conversion is lower when compared with reactions under aerobic conditions (Table 2), but the complexes [Ni(salen)] and [Ni(salhd)] still present the highest values (62 and 65%, respectively) followed by [Ni(α,α' -Me₂salen)] (48%) and finally [Ni(3-MeOsalen)] (47%). On the other hand, the epoxide selectivity increases for all complexes except for the [Ni(3-MeOsalen)]-catalysed reaction. As observed for the reactions in the presence of oxygen, the highest epoxide selectivity was obtained for [Ni(α,α' -Me₂salen)], whereas [Ni(3-MeOsalen)] shows the lowest value. The dependency of the epoxide selectivity on the ligand is noteworthy, and is more significant when oxygen is absent.

Overall, the alkene conversion is higher and the reaction faster in the presence of oxygen, although the epoxide selectivity is higher in the absence of oxygen.

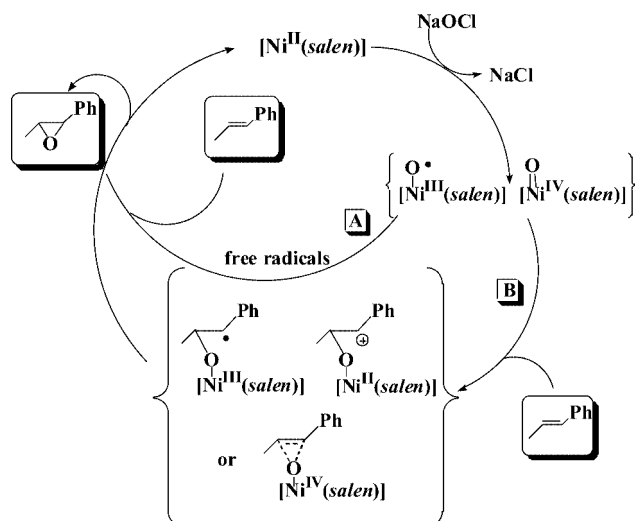
Reaction Mechanism

Salen-type complexes have been used in epoxidation reactions owing to their special coordination environment, which, like porphyrins, provides a square-planar geometry around the metal atom that allows reactants and/or oxidant to access the active centre. Although the oxidation mechanism through which the metal complexes act in an oxi-

dation reaction is not completely understood, it is known that the reaction selectivity depends on how the oxygen atom is transferred to the alkene. A rebound mechanism involving the formation of a (oxo)metal intermediate and alkyl radicals has been proposed for Cytochrome P450, a (porphyrin)iron compound.^[27] Recently, it has been proved that these short-lived radicals are mainly free in solution rather than being bound to the (oxo)metal species.^[28]

The involvement of an (oxo)metal species of high oxidation state ($M^{n+}=O$; $n = 3, 4$ or 5) has also been proved for (salen)manganese- and -chromium-catalysed epoxidations.^[29] In the case of the (salen)nickel-catalysed epoxidations, the formation of an (oxo)metal intermediate is consistent with the dependency of the alkene conversion with the ligand type, although, as suggested by Burrows and co-workers, another intermediate with a radical character can also be formed, namely $Ni^{III}-O^{\cdot}$. This species can instigate the formation of free radicals that compete in the oxidation of the substrate and, therefore, result in reactions with low epoxide selectivity (Scheme 2, mechanism A).^[6,9] Alternatively, the alkene can bind to the (oxo)metal intermediate and different paths can then follow (Scheme 2, mechanism B).^[30] In the case of epoxidations catalysed by (cyclam)nickel complexes, two main pathways have been suggested for the subsequent steps: (1) a concerted mechanism in which the substrate-(oxo)metal intermediate suffers a heterolytic cleavage leading to the desired epoxide, and (2) a stepwise pathway implying the formation of a carbocation or a carbon radical, which forms the product by homolytic cleavage. The heterolytic cleavage is known to afford high yields of epoxide, while the other preferably performs allylic oxidations;^[31] both are summarised in Scheme 2.

On the basis of the catalytic results obtained in the absence and presence of oxygen, the formation of free radicals (mechanism A) cannot be excluded. Free radicals can capture oxygen and consequently enhance the reaction rate and alkene conversion;^[32,33] therefore, a free-radical mechanism would explain the higher rates and alkene conversions observed for the reactions run under oxygen. On the other hand, the dissimilarity in product selectivity obtained with different complexes in the absence of oxygen points to the involvement of a substrate-(oxo)metal intermediate (mechanism B), which, through a concerted or a stepwise



Scheme 2. Proposed mechanism for the *trans*-β-methylstyrene epoxidation by NaOCl with (salen)nickel(II) complexes.

mechanism, allows a good proximity of the substrate to the ligand. Also, as the carbon radical formed in the stepwise pathway in mechanism B is expected to be very sensitive to the presence of O₂, resulting in highly oxidised products (such as benzaldehyde), this mechanism could explain the lower epoxide selectivity observed in the reactions run in the presence of oxygen.

The substantially lower epoxide selectivity obtained with the complex that bears electron-donor substituents, [Ni(3-MeOsalen)], in the absence of oxygen is noteworthy. Studies on the epoxidation of alkenes by (salen)chromium complexes have shown that complexes bearing methoxy groups in the *ortho*-position to the hydroxy group of the salicylaldehyde moiety are easily destroyed by the oxidant.^[34]

In this context, our results support the occurrence of two competitive mechanisms (Scheme 2): a mechanism where the (oxo)metal species originates free radicals that, in the presence of oxygen, cause higher and faster alkene conversions but indistinguishable epoxide selectivity (mechanism A), and a mechanism involving binding of the substrate to the (oxo)metal intermediate that, through a concerted or a stepwise pathway, results in lower conversions, but higher epoxide selectivity (mechanism B).

Mechanism A is favoured in the presence of oxygen, while mechanism B is favoured in its absence.

Heterogeneous Catalysis

To study the catalytic activity of the immobilised nickel(II) complexes, the epoxidation of *trans*-β-methylstyrene by NaOCl was carried out using the prepared materials as heterogeneous catalysts. The reactions were run under the same conditions as described for the homogeneous phase, using an amount of zeolite corresponding to the same substrate/catalyst ratio (1:0.025) in dichloromethane (see Exp. Sect.). As in the homogeneous phase, the reactions were performed in the presence and in the absence of oxygen.

Table 3 summarises the results obtained in the heterogeneous phase using the nickel complexes immobilised in zeolites X and Y, in the presence of oxygen.

Table 3. Results obtained for the heterogeneous catalysis in the presence of oxygen.^[a]

Catalyst	Conv. [%] ^[b]	Selectivity [%] (Yield [%])		
		Epoxide ^[c]	Benzaldehyde	Others
[Ni(salen)]@X	71	40 (28)	23 (16)	37 (26)
[Ni(salhd)]@X	27	28 (8)	27 (7)	45 (12)
[Ni(α,α'-Me ₂ salen)]@X	88	53 (47)	15 (13)	32 (28)
[Ni(3-MeOsalen)]@X	19	22 (4)	36 (7)	42 (8)
[Ni(salen)]@Y	30	34 (10)	16 (5)	50 (15)
[Ni(salhd)]@Y	44	48 (21)	23 (10)	28 (12)
[Ni(α,α'-Me ₂ salen)]@Y	62	45 (28)	22 (14)	33 (20)
[Ni(3-MeOsalen)]@Y	19	25 (5)	60 (11)	15 (3)

[a] Solvent: CH₂Cl₂; alkene/catalyst ratio = 1.0:0.025; results after 48 h. [b] Conversion (as disappearance of alkene) determined by GC using *n*-decane as internal standard. [c] Obtained as 100% *trans*-epoxide.

The reaction time increased significantly and thus the results in Table 3 refer to values obtained after 48 h. The results show that all the immobilised complexes are active in the epoxidation of the alkene, but the catalytic activity is lower than in the homogeneous reactions. The reactions catalysed by zeolites with [Ni(α,α'-Me₂salen)], which reached conversions close to those obtained in the homogeneous phase, are excluded from this conclusion. In fact, the maximum conversion (88%) among the heterogeneous catalysts was observed for [Ni(α,α'-Me₂salen)]@X, together with the highest epoxide selectivity.

Lower conversions and longer reactions times are usually observed on going from solution to immobilised catalysts due to the diffusion constraints imposed by the pore network.^[18] Although the solid support can constitute a protective environment around the metal atom, the physical restrictions imposed by the zeolite can make the access of reactants to the metal centre more difficult and, as a result, the activity decreases.

In this case, a correlation between the catalytic activity of the complexes and their distribution within the solids confirms the effect of diffusion constraints: the complexes localised in the outer layers of the zeolites (see above), which therefore can be more easily accessed by the reactants, give higher catalytic activities.

Surprisingly, the epoxide selectivity was lower in all the heterogeneous reactions than in the homogeneous phase, resulting in higher benzaldehyde selectivity. The chemical microenvironment imposed by the zeolites could be the cause of this result. Epoxide ring opening in acidic media forms benzaldehyde, thus the acid character of the zeolites contributes to the lowering of the epoxide selectivity. Again, the zeolites that bear complexes closer to the surface, such as [Ni(α,α'-Me₂salen)]@X and [Ni(α,α'-Me₂salen)]@Y, are less affected by the zeolite characteristics and present nearly the same epoxide selectivity as in the homogeneous phase.

The effect of the zeolites' acidity in the reaction selectivity can be noted by comparing the epoxide selectivity ob-

tained for a complex immobilised in zeolite X with the same complex immobilised in zeolite Y (Table 3). Apart from the other factors already discussed in this paper, the complexes in zeolite X have a higher epoxide selectivity than the complexes in Y, a zeolite with more acidic sites.

The activity of the immobilised catalysts was also evaluated in the absence of oxygen and the results are collected in Table 4. As observed for the homogeneous phase, the absence of oxygen results in lower conversions and higher epoxide selectivity, except for [Ni(3-MeOsalen)], which registers an increase in the conversion when compared with the reaction run under oxygen. Once more, as observed for the homogeneous system, this is the complex with the lowest epoxide selectivity, due to its fast decomposition in the reaction media.

Table 4. Results obtained for the heterogeneous catalysis in the absence of oxygen.^[a]

Catalyst	Conv. [%] ^[b]	Selectivity [%] (Yield [%])		
		Epoxide ^[c]	Benzaldehyde	Others
[Ni(salen)]@X	62	60 (37)	13 (8)	28 (17)
[Ni(salhd)]@X	13	41 (5)	7 (1)	52 (7)
[Ni(α,α' -Me ₂ salen)]@X	62	59 (37)	12 (7)	29 (18)
[Ni(3-MeOsalen)]@X	39	46 (18)	14 (5)	40 (16)
[Ni(salen)]@Y	48	60 (29)	18 (9)	22 (11)
[Ni(salhd)]@Y	43	59 (25)	14 (6)	27 (12)
[Ni(α,α' -Me ₂ salen)]@Y	64	64 (41)	16 (10)	20 (13)
[Ni(3-MeOsalen)]@Y	32	38 (12)	31 (10)	31 (10)

[a] Solvent: CH₂Cl₂; alkene/catalyst ratio = 1.0:0.025; results after 48 h. [b] Conversion (as disappearance of alkene) determined by GC using *n*-decane as internal standard. [c] Obtained as 100% *trans*-epoxide.

The catalytic activity in the heterogeneous phase follows the same pattern as the homogeneous-phase reactions, hence we propose that the conclusions concerning the reaction mechanism drawn for the homogeneous system can be extended to the heterogeneous counterpart. In this context, the two mechanisms presented above are also competing in the heterogeneous reaction: a mechanism involving the formation of free radicals and a mechanism occurring through a substrate-(oxo)metal intermediate.

Re-Use of Heterogeneous Catalysts

The possibility to re-use [Ni(3-MeOsalen)]@X and [Ni(3-MeOsalen)]@Y was evaluated in the subsequent way: after the first run, the catalysts were filtered from the solution, washed with copious amounts of dichloromethane, dried and re-used according to the general procedure described for the heterogeneous reactions. The results of the re-utilisation and the relation with the first use are illustrated in Figure 5.

For [Ni(3-MeOsalen)]@X, the conversion is similar to that obtained in the first use (19%), but the epoxide selectivity shows a significant increase from 22% to 53%. In the case of [Ni(3-MeOsalen)]@Y, an increase in both conversion (from 19 to 30%) and epoxide selectivity (from 25 to 46%) was observed.

The immobilised catalysts show similar conversions in their re-use compared to their first utilisation: the conversion is equal or even higher than in the first use and there is an increase in the epoxide selectivity. These positive results can be attributed to a change in the overall chemical environment around the complex. In the first use the materials are in contact with NaOCl and a chemical modification from acidic to more basic environment might have occurred. This effect is more significantly reflected in the reactions catalysed by the zeolite with higher initial acidity (zeolite Y). Also, a possible migration of the complex to the outer surface layers of the zeolites cannot be excluded; this decreases the diffusion constraints and therefore favours an increase in conversion.

However, as [Ni(3-MeOsalen)] suffers decomposition in both homogeneous and heterogeneous media, additional experiments should be performed to reach safer conclusions about the catalysts' re-utilisation.

Conclusions

All the (salen)nickel(II) complexes are active catalysts in the epoxidation of *trans*- β -methylstyrene by NaOCl in homogeneous media, both in the presence and in the ab-

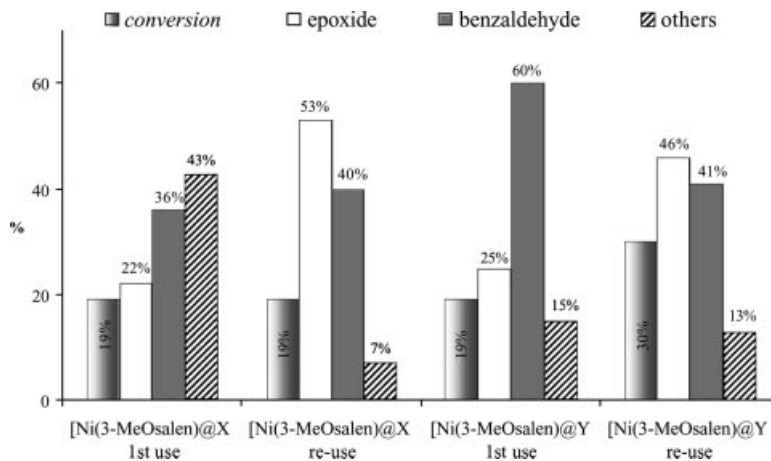


Figure 5. Conversion and selectivity obtained in the first use and in the re-use of [Ni(3-MeOsalen)]@X and of [Ni(3-MeOsalen)]@Y in the epoxidation of *trans*- β -methylstyrene by NaOCl.

sence of oxygen. Conversions of up to 100% and epoxide selectivity of around 54% are obtained in the presence of oxygen. However, in the absence of oxygen, the reaction is slower, with lower conversions but with higher epoxide selectivity.

These results lead to a proposal of two simultaneous mechanisms for this reaction: a mechanism implying the formation of free radicals, which is favoured in the presence of oxygen, in competition with a mechanism where the substrate binds to an (oxo)metal intermediate. The first would lead to higher alkene conversions but lower and indistinguishable epoxide selectivity, while the other would result in higher epoxide selectivity dependent on the ligand, but lower conversions.

The immobilisation of the four nickel complexes in zeolites X and Y results in materials with different loading and distribution of the complexes. Complexes [Ni(salhd)] and [Ni(3-MeOsalen)] have higher loadings than [Ni(α,α' -Me₂-salen)] and [Ni(salen)]. The former are also more uniformly distributed than the latter, which are preferentially localised in the surface layers of the zeolites.

All the materials are active catalysts in the epoxidation of *trans*- β -methylstyrene by NaOCl, both in the presence of oxygen and in its absence, but the conversions are lower than in the homogeneous phase. The zeolites bearing the metal complexes closer to the surface give higher conversions than those having higher loadings, but a more uniform distribution of the complexes. These results can be explained by the physical restrictions imposed by the zeolite pore network, which makes the access of the reactants to the metal centre more difficult, resulting in lower activities. Furthermore, the zeolite chemical environment, namely its acidic character, influences the selectivity of the reaction. Nevertheless, the zeolites can constitute an important protective environment around the ligand and an opportunity to improve the catalyst life, i.e., by catalyst re-utilisation.

Experimental Section

Reagents and Solvents: The solvents used in the preparation of the complexes were of reagent grade and were used as received. Dichloromethane used in the epoxidation reactions was HPLC grade. An aqueous solution of NaOCl (available chlorine 10–13%, Aldrich) was used as oxidant. Salicylaldehyde, 2-hydroxy-3-methoxybenzaldehyde, 2'-hydroxyacetophenone and the diamines 1,2-cyclohexanediamine (as *cis/trans* mixture) and ethylenediamine were purchased from Aldrich. The substrate *trans*- β -methylstyrene was also purchased from Aldrich and *n*-decane was obtained from Fluka. Nickel acetate, nickel nitrate pentahydrate and sodium hydrogen phosphate were obtained from Merck. All reagents were used with no further purification, except the diamines, which were distilled prior to use. The GC standard epoxide was prepared by epoxidation of *trans*- β -methylstyrene with *m*-chloroperbenzoic acid (*m*-CPBA) at 4 °C and stored at that temperature. The phase-transfer catalyst benzyltributylammonium bromide was obtained from Fluka. The zeolites in their sodium form, NaY and NaX, were kindly provided by Grace GmbH (Germany) and were calcinated at 600 °C under oxygen before use.

Instrumentation: Silicon, aluminium, sodium and nickel contents were determined by Kingston Analytical Services (UK) by ICP-

AES. The samples were previously treated by fusion with LiBO₂ and the mixture dissolved in nitric acid. Surface chemical analysis of the materials was performed by X-ray photoelectron spectroscopy at the Centro de Materiais da Universidade do Porto (Portugal) in a VG Scientific ESCALAB 200A spectrometer, using Mg-*K_α* radiation (1253.6 eV). Electronic spectra were recorded with a Shimadzu UV/3101PC spectrophotometer equipped with a BaSO₄ sphere and using the same salt as reference. FTIR spectra were recorded from KBr pellets of the materials or complexes with a JASCO FT/IR-460 Plus spectrometer. GC analysis was carried out with a Varian 3400 CX equipped with a fused silica Chrompack capillary column (30 m × 0.53 mm) and a TCD detector. The column temperature was programmed from 60 °C (3 min) to 170 °C, at a rate of 5 °C min⁻¹, and the injection temperature was 200 °C.

General Procedure for the Synthesis of Nickel Complexes: The ligands H₂salen, H₂(salhd), H₂(α,α' -Me₂salen) and H₂(3-MeOsalen) and the respective nickel(II) complexes *N,N'*-bis(salicylidene)-1,2-diamine, [Ni(salen)] (1), *N,N'*-bis(salicylidene)-1,2-cyclohexenediamine, [Ni(salhd)] (2), *N,N'*-bis(α -methylsalicylidene)-1,2-diamine [Ni(α,α' -Me₂salen)] (3) and *N,N'*-bis(3-methoxysalicylidene)-1,2-diamine, [Ni(3-MeOsalen)] (4) (Scheme 1) were prepared and fully characterised in refs.^[35,36] according to standard procedures.^[37]

General Procedure for the Preparation of the Immobilised Catalysts: The preparation of the immobilised (salen)nickel complexes followed the “ship-in-a-bottle” procedure^[23] using the “flexible ligand” method. In a typical preparation, a suspension of calcinated NaY or NaX (10 g) in an aqueous solution containing Ni(NO₃)₂ (6 mmol) was heated at 70–80 °C for 24 h. The solid was then filtered and dried at 120 °C under vacuum, and the ion-exchanged zeolite (2 g; NiY or NiX) was mixed with the corresponding ligand (metal/ligand molar ratio = 1:2) and heated to 130–150 °C for 2 h. A change in the colour of the material from pale green (characteristic of hexahydrated Ni^{II}) to orange-brown [typical of (salen)Ni^{II} complexes] confirmed complex formation. The solids were then purified by solid-liquid Soxhlet extraction with appropriate solvents (dichloromethane or ethanol) to remove unreacted ligands and surface-bound complexes. The materials were denoted as [Ni(salen)]@X, [Ni(salhd)]@X, [Ni(α,α' -Me₂salen)]@X [Ni(3-MeOsalen)]@X, [Ni(salen)]@Y, [Ni(salhd)]@Y, [Ni(α,α' -Me₂salen)]@Y and [Ni(3-MeOsalen)]@Y.

General Procedure for the Epoxidation Reactions: In a typical experiment, a solution of the oxidant (5 mL) buffered to pH = 11 (with a solution of Na₂HPO₄) was stirred at room temperature in a solution of dichloromethane (5 mL) enriched with *trans*- β -methylstyrene (2 mmol), the nickel catalyst (0.05 mmol) (substrate/catalyst = 1:0.025) and benzyltributylammonium bromide (0.06 mmol), used as phase-transfer agent. A similar procedure was employed for the heterogeneous reactions using an amount of material corresponding to a substrate/nickel complex ratio of 1:0.025. In this case the catalysts were first activated at 120 °C for 2 h just before use and no phase-transfer agent was employed. The reactions were run at room temperature with continuous magnetic stirring and were followed by GC using *n*-decane as internal standard. For the reactions carried out in the absence of oxygen, the solvent was first deoxygenated with argon for some minutes in a Schlenk tube, and the reaction was run under argon.

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- [1] L. Canali, D. C. Sherrington, *Chem. Soc. Rev.* **1999**, 28, 85–93.
- [2] E. N. Jacobsen, A. Pfaltz, H. Yamamoto, *Comprehensive Asymmetric Catalysis*, Springer, Berlin, **1999**, vol. III.
- [3] H. Nishikori, C. Ohta, T. Katsuki, *Synlett* **2000**, 1557–1560.
- [4] M. J. Sabater, A. Corma, A. Domenech, V. Fornés, H. García, *Chem. Commun.* **1997**, 1285–1286.
- [5] J. F. Kinneary, T. R. Wagner, C. J. Burrows, *Tetrahedron Lett.* **1988**, 29, 877–880.
- [6] J. F. Kinneary, J. S. Albert, C. J. Burrows, *J. Am. Chem. Soc.* **1988**, 110, 6124–6129.
- [7] R. I. Kureshy, N. H. Khan, S. H. R. Abdi, P. Iyer, A. K. Bhatt, *J. Mol. Catal. A: Chem.* **1998**, 130, 41–50.
- [8] R. I. Kureshy, N. H. Khan, S. H. Abdi, S. t. Patel, P. Iyer, E. Suresh, P. Dastidar, *J. Mol. Catal. A: Chem.* **2000**, 160, 217–227.
- [9] H. Yoon, C. J. Burrows, *J. Am. Chem. Soc.* **1988**, 110, 4087–4089.
- [10] H. Yoon, T. R. Wagner, K. J. O'Connor, C. J. Burrows, *J. Am. Chem. Soc.* **1990**, 112, 4568–4570.
- [11] R. A. Sheldon, R. S. Downing, *Appl. Catal. A* **1999**, 189, 163–183.
- [12] J. M. Thomas, T. Maschmeyer, B. F. G. Johnson, D. S. Shepard, *J. Mol. Catal. A: Chem.* **1999**, 141, 139–144.
- [13] R. Ferreira, M. Silva, C. Freire, B. de Castro, J. L. Figueiredo, *Microporous Mesoporous Mater.* **2000**, 38, 391–401.
- [14] A. R. Silva, M. Martins, M. M. A. Freitas, J. L. Figueiredo, C. Freire, B. de Castro, *Eur. J. Inorg. Chem.* **2004**, 2027–2035.
- [15] R. Ferreira, C. Freire, B. de Castro, A. P. de Carvalho, J. Pires, M. Brotas de Carvalho, *Eur. J. Inorg. Chem.* **2002**, 3032–3038.
- [16] I. Kuzniarska-Biernacka, A. R. Silva, R. Ferreira, A. P. de Carvalho, J. Pires, M. Brotas de Carvalho, C. Freire, B. de Castro, *New J. Chem.* **2004**, 28, 853–858.
- [17] A. R. Silva, J. L. Figueiredo, C. Freire, B. de Castro, *Microporous Mesoporous Mater.* **2004**, 68, 83–89.
- [18] A. R. Silva, C. Freire, B. de Castro, *Carbon* **2004**, 42, 3003–3042.
- [19] M. R. Maurya, S. J. J. Titinchi, S. Chand, *J. Mol. Catal. A: Chem.* **2003**, 201, 119–130.
- [20] D. Chatterjee, A. Mitra, *J. Mol. Catal. A: Chem.* **1999**, 144, 363–367.
- [21] D. Chatterjee, S. Mukherjee, A. Mitra, *J. Mol. Catal. A: Chem.* **2000**, 154, 5–8.
- [22] V. Ayala, A. Corma, M. Iglesias, J. A. Rincón, F. Sanchez, *J. Catal.* **2004**, 224, 170–177.
- [23] A. Corma, H. García, *Eur. J. Inorg. Chem.* **2004**, 1143–1164.
- [24] V. Crupi, D. Majolino, V. Venuti, *J. Phys. Condens. Matter* **2004**, 16, S5297–S5316.
- [25] V. Ramaswamy, M. Sivarama, K. Krishnan, A. V. Ramaswamy, *J. Mol. Catal. A* **2002**, 181, 81–89.
- [26] Mainly chlorinated and allylic hydroxylation products (identified by GC-MS).
- [27] J. T. Groves, G. A. McClusky, *J. Am. Chem. Soc.* **1976**, 98, 859–861.
- [28] S. Shaik, S. Cohen, S. P. de Visser, P. K. Sharma, D. Kumar, S. Kozuch, F. Ogliaro, D. Danovich, *Eur. J. Inorg. Chem.* **2004**, 207–226.
- [29] C. T. Dalton, K. M. Ryan, V. M. Wall, C. Bousquet, D. G. Gilheany, *Top. Catal.* **1998**, 5, 75–91.
- [30] A. M. Daly, M. F. Renahan, D. G. Gilheany, *Org. Lett.* **2001**, 3, 663.
- [31] W. Adam, K. J. Roschmann, C. R. Saha-Möller, D. Seebach, *J. Am. Chem. Soc.* **2002**, 124, 5068–5073.
- [32] For this reason, in certain oxidations using peroxides, such as the Fenton reaction, H_2O_2 is often seen as an initiator rather than an oxidant because it contributes only to initiate the formation of radicals from O_2 . It is therefore interesting to explore the catalytic activity of the complexes in the absence of oxygen.
- [33] W. R. Sanderson, *Pure Appl. Chem.* **2000**, 72, 1289–1304.
- [34] K. M. Ryan, C. Bousquet, D. G. Gilheany, *Tetrahedron Lett.* **1999**, 40, 3613–3616.
- [35] C. Freire, B. de Castro, *J. Chem. Soc., Dalton Trans.* **1998**, 1491–1497.
- [36] C. Freire, B. de Castro, *Polyhedron* **1998**, 17, 4227–4235.
- [37] R. H. Holm, G. W. Everett Jr., A. Chakravorty, in *Progress in Inorganic Chemistry* (Ed.: F. A. Cotton), John Wiley and Sons, New York, **1966**, vol. 7, p. 183.

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