Catalytic activity of Jacobsen catalyst encapsulated in an alumina matrix by the sol–gel process

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Abstract

This work describes optimized conditions for the preparation of the Jacobsen catalyst entrapped in alumina in the powder form. The hybrid material was obtained by a non-hydrolytic sol–gel route, through condensation of aluminum chloride with diisopropylether in the presence of the Jacobsen catalyst. The material was characterized by X-ray diffraction (XRD), surface area analysis, thermogravimetric analysis (TG), differential thermal analysis (DTA), and ultraviolet–visible spectroscopy. The ultraviolet–visible absorption spectrum of the entrapped catalyst displayed the typical bands of the Jacobsen catalyst, showing that the structure of the complex was preserved in the hybrid material. This material efficiently catalyzed the oxidation of (Z)-cyclooctene, styrene, and cyclohexane by different oxidants (iodosylbenzene, iodosylbenzenediacetate, 3-chloroperoxybenzoic acid, *tert*-butyl hydroperoxide, hydrogen peroxide 30 and 70 wt.%) when compared with the catalyst in homogeneous solution. These results show the importance of the non-hydrolytic alumina matrix in making the Jacobsen catalyst more active, avoiding its destruction and/or the formation of dimeric specie.

1. Introduction

Dissymmetric Schiff-base metal chelates are among the most widely studied compounds to be used as catalysts for the enantioselective epoxidation of unfunctionalized alkenes. Good overall epoxide yields have been obtained with a variety of olefin substrates and oxygen atom sources by using manganese salen complexes such as the Jacobsen catalyst, Mn(salen) (Fig. 1) [1–11]. However, the utility of these Mn(salen) catalysts has been limited by the relatively easy catalyst deactivation that is thought to occur primarily by formation of the Mn(IV) μ-oxo dimer [12]. One approach to overcoming this problem has been centered around the site isolation of Mn(salen) through its entrapment in to zeolites, mesoporous materials, silica, and alumina [13–15].

Sol–gel routes allow the entrapment of inorganic catalysts into a porous matrix with production of designed microstructures at low temperature, resulting in hybrid materials with intrinsic properties [16,17]. However, conventional sol–gel routes involve the hydrolysis and condensation of metal alkoxides under controlled pH conditions, making the obtention of homogeneity at the molecular level difficult because of the different reactivities of the various precursors. An alternative and highly effective method for the preparation of heterogeneous catalysts is the use of non-hydrolytic processes to synthesize multicomponent oxides. In these processes, metal halides can react with metal alkoxides through the *in situ* formation of an alkyl halide [18,19]. This approach is attractive because it isolate the catalytic complex, thus avoiding catalyst inactivation by aggregation or self-oxidative destruction. Another feature that is

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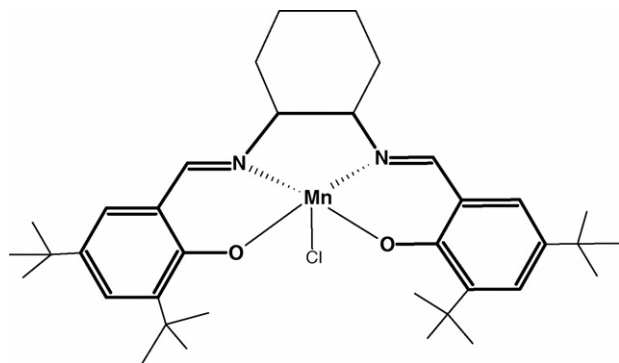*E-mail address:* mddassis@usp.br (M.D. Assis).

Fig. 1. The Jacobsen catalyst.

pursued in these catalysts is their easy recovery from the reaction medium and their recycling.

Alumina is typically used as a support or as a catalyst for a variety of substrates because it is a non-polluting compound and it is possible to use it in the presence of environmentally friendly oxidants [20]. Alumina has also been successfully applied to the entrapment of catalysts, such as metalloporphyrins [21], rare earth ions [22], and nickel and cobalt complexes [16,19].

In a previous work, Lima et al. [21] reported that the catalytic activity of second generation metalloporphyrins was improved when these systems were entrapped in an alumina sol–gel matrix prepared by non-hydrolitic sol–gel methodology. In order to build systems useful for large-scale applications, it would be interesting to use salen complexes, like the simple Jacobsen catalyst, which is cheap and whose synthesis and purification are easy, supported on an easy-to-handle-and-recycle matrix. Therefore, the purpose of the present work is to develop a simple method for the preparation of an efficient heterogeneous catalyst consisting of Mn(salen) entrapped in an alumina matrix, by a non-hydrolytic sol–gel route. The new hybrid material, Mn(salen)-NHG, was used as catalyst in the oxidation of cyclohexane, (Z)-cyclooctene and styrene by different oxidants.

2. Experimental

2.1. Materials

The Jacobsen catalyst was purchased from Acros Organics and used as received. Acetonitrile (ACN) was acquired from J.T. Baker. Dichloromethane (DCM) was suspended over anhydrous $CaCl_2$ for 2.5 h, then filtered and distilled over P_2O_5 and stored over 0.4 nm molecular sieves. Alkenes (Z-cyclooctene and styrene) were purified in a short activated alumina column (Merck) immediately before use. *Tert*-butyl hydroperoxide (*t*-BuOOH), 70 wt.% solution in water, was acquired from Acros Oganics and hydrogen peroxide, 30 and 70 wt.%, was obtained from Fluka and Peróxidos do Brasil, respectively, Iodosylbenzene (PhIO) was obtained through the hydrolysis of iodosylbenzenediacetate [23]. Its purity was measured by iodometric assay [23]. Iodosylbenzenediacetate (IBDA) and 3-chloroperoxybenzoic acid (m-CPBA) were purchased from Acros Oganics.

2.2. Preparation of the Jacobsen catalyst entrapped in alumina by a non-hydrolytic sol–gel process (Mn(salen)-NHG)

The preparation of the gels was carried out in oven dried glassware. The material was synthesized via a modification to the method described by Corriu [24]. Aluminum chloride (1.0 mol L^{-1}) and diisopropyl ether [(iPr)$_2$O, 1.5 mol L^{-1}] were reacted in the presence of the Jacobsen catalyst (3.5 mg, 8.7×10^{-6} mol) by refluxing at 110 °C in dry DCM (50 mL, previously distilled), under argon atmosphere. The condenser was placed in a thermostatic bath at −8 °C. A gel was formed after 4 h of reaction and, after another 0.5 h, a solid material started to precipitate. After reflux, the mixture was cooled and aged overnight in the mother liquor at room temperature. The solvent was then removed under vacuum. The solid was washed with several solvents (in the following order: DCM, acetonitrile, and methanol), and heat-treated at 110 °C. Jacobsen catalyst loading on the support was determined using UV–vis spectroscopy to measure the amount of Jacobsen complex in the combined washings.

2.3. Characterization of the catalytic system

The electronic spectra of the Mn(salen)-NHG material were recorded on a UV–vis spectrophotometer (Hewlett-Packard 8453, Diode Array). The spectra of the solid in DCM were recorded in a 2.0 mm path length cell. Better quality spectra were obtained by using dichloromethane as solvent when the suspension was prepared. Specific surface areas were determined by analyzing the nitrogen adsorption isotherms according to the BET method [25] on a physical adsorption analyser (Micrometrics AccSorb 2100E). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a Thermal Analyst TA Instrument SDT Q 600 Simultaneous DTA–TGA–DSC, in nitrogen, at a heating rate of 10 °C/min, from 25 to 850 °C. XRD patterns were collected on a Siemens model D 5005 diffractometer using Cu Kα radiation.

2.4. Oxidation reaction

The encapsulated Mn(salen)-NHG (2.5×10^{-8} mol) was stirred with (Z)-cyclooctene, styrene, or cyclohexane and the oxidant (PhIO, IBDA, m-CPBA, *t*-BuOOH, H_2O_2 30% and H_2O_2 70%) in acetonitrile (1.5 mL). The catalyst:oxidant:substrate molar ratio was 1:1000:20 000. All the reactions were carried out at room temperature with magnetic stirring.

Reactions in the absence of oxygen were carried out in a flask sealed with a septum. The Mn(salen)-NHG or neat complex and iodosylbenzene were thoroughly flushed with argon prior to the addition of the substrate and ACN, which had also been previously thoroughly flushed with argon.

The internal standard (bromobenzene) was added and the products were analyzed by gas chromatography on a Varian Star 3400 CX chromatograph, using a flame ionization detector and a DB-wax (1 μm thickness) megabore column

(30 m × 0.538 mm). Nitrogen was used as the carrier gas. The results were recorded and processed on a Varian Workstation. The products were analyzed by comparison of their retention times with those of authentic samples. The yields are based on the added oxidant and were determined after 8 h of reaction by using bromobenzene as internal standard.

The stability of Mn(salen)-NHG was investigated in repeated reactions carried out in acetonitrile (1.5 mL) using 2.5×10^{-8} mol of catalyst and 5.0×10^{-4} mol of substrate (cyclooctene and styrene). These reactions were monitored for six additions of PhIO, IBDA, m-CPBA and H_2O_2 70% (2.5×10^{-5} mol per addition), added at 24-h intervals. The yields were determined based on oxidant added per addition.

Recycling of the supported catalyst was carried out with the solid recovered after oxidation reaction by filtration, washing with methanol and drying.

Control reactions were carried out in the absence of the catalyst and in the presence of NHG alumina alone.

3. Results and discussion

3.1. Synthesis of the sol–gel powder materials

The preparation of the oxide materials using non-hydrolytic condensation reactions is well-documented. Alumina non-hydrolytic gels were first prepared through the methodology described by Corriu et al. [24], by means of the reaction of equimolar amounts of aluminum halide and aluminum alkoxide [reaction (1)], where the alkoxide can be added to the reaction medium or produced *in situ* from $AlCl_3$ and $(iPr)_2O$. When a solution of $AlCl_3$ and $(iPr)_2O$ is heated, a monolithic alumina gel is formed, followed by precipitation of an alumina powder:

$$AlX_3 + (3/2)ROR \rightarrow AlO_{3/2} + 3RX,$$

$$RX = \text{residual alkyl halide groups} \qquad (1)$$
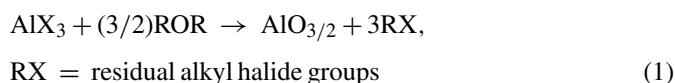
The Mn(salen)-NHG material was prepared by adding the Jacobsen catalyst to a starting solution of $AlCl_3$ and $(iPr)_2O$. Heating the solution in the presence of the salen complex led to the formation of an alumina gel containing the Mn(salen) complex confined in its skeleton (Fig. 2). When the alumina powder precipitated, the Mn(salen) complex remained entrapped inside the alumina network. At this point, the network was supple and further condensation and bond formation occurred during the aging in the reaction solution and also during the slow solvent removal. This stage was of great importance to consolidate the alumina network and the new formed bonds helped restrain the Mn(salen) complex entrapped in the alumina network. After aging, the solid was washed with several solvents (in the following order: DCM, acetonitrile, and methanol) until the UV–vis spectra of the reaction solution did not present the bands typical of the Mn(salen) complex, which indicated that the Jacobsen catalyst was entrapped in the NHG matrix and resulted in solid Mn(salen)-NHG as a yellow powder. Since the pure non-hydrolytic alumina gel is white, the yellow color of the Mn(salen)-NHG must have been conferred by the presence of the entrapped Jacobsen catalyst in this material.
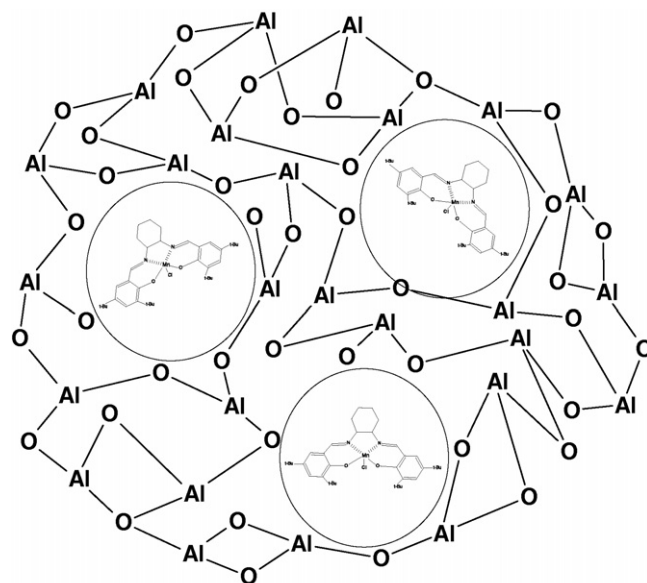

Fig. 2. Schematic view of the Jacobsen catalyst in the alumina matrix.

The Mn(salen)-NHG material exhibited UV–vis spectrum characteristic of the Jacobsen catalyst, with absorptions at 325 and 438 nm (Fig. 3). The band at 328 nm is attributed to the $n \rightarrow \pi^*$ transition of the azomethine chromophore, and the band at 440 nm is attributed to the $d \rightarrow d$ transition [26]. The similarity between the UV–vis spectra of both the complex in solution and entrapped in alumina indicates that the structure of the complex was preserved in the matrix, corresponding to a catalyst loading of 2.5×10^{-6} mol/g of the solid as indirectly determined by measuring the concentration of this complex in the washing solvents.

The choice of the non-hydrolytic alumina gel process to synthesize the hybrid material was of great importance, since the conventional hydrolytic sol–gel process leads to the complete leaching of complexes from the matrix [16,27].

It is well known that the introduction of homogeneous catalysts or metals into porous supports leads to a decrease in the specific surface area and pore volume of the supporting material. Data concerning the porosity and surface properties of
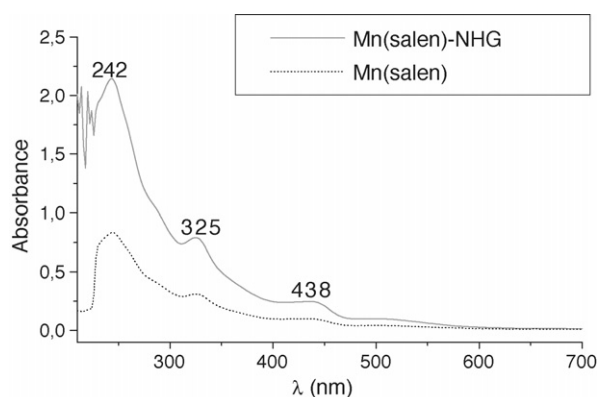

Fig. 3. UV–vis spectra of Mn(salen) in acetonitrile and Mn(salen)-NHG. The alumina matrix alone was used as reference for Mn(salen)-NHG. Black line Mn(salen)-NHG; dashed line Mn(salen).

Table 1
BET surface area and pore volumes of alumina (NHG) and Mn(salen)-NHG

Sample	S_{BET} ($m^2 g^{-1}$)	Pore volume ($ml g^{-1}$)
Alumina (NHG)	99.8	0.183
Mn(salen)-NHG	31.2	0.088

Mn(salen)-NHG and the alumina support are shown in Table 1. The alumina support has a higher surface area, 99.8 $m^2 g^{-1}$, and a pore volume of 0.183 $ml g^{-1}$. After metal complex functionalization, the surface area decreased to 31.2 $m^2 g^{-1}$, which is in agreement with the surface area reported in the literature for Co/alumina systems, which have surface area between 1 and 45 $m^2 g^{-1}$ [19]. The decrease in the mesoporous volume (~52%, Table 1) and surface area (~68%, Table 1) indicate that the Jacobsen catalyst was really entrapped in the alumina matrix. Nitrogen adsorption isotherms of the material were typical of the type II isotherm, according to the BDDT classification [28]. The hysteresis loop in the isotherms changed according to the temperature at which the sample was heat-treated. Mn(salen)-NHG heat-treated at 110 °C displayed an H3-type hysteresis loop, according to the IUPAC classification.

The X-ray powder diffraction (XRD) patterns of the alumina blank (without catalyst) and Mn(salen)-NHG were recorded at 2θ values ranging between 5° and 70°. In all the cases, the typical diffraction pattern of amorphous samples was observed. Analysis of the diffractograms revealed that immobilized Mn(salen)-NHG has structural characteristics similar to those of the alumina without catalyst. Thus, the immobilization process did not change the diffraction amorphous pattern of the alumina support.

The TGA–DTG–DTA data of Mn(salen) and Mn(salen)-NHG materials are shown in Fig. 4A and B, respectively. The TGA–DTG curves showed that weight losses occurred mainly between 20 and 600 °C, corresponding to a 60 and 50% weight loss for Mn(salen) and Mn(salen)-NHG, respectively.

The initial weight loss observed for the Mn(salen)-NHG material (Fig. 4B), from 20 to 230 °C, accomplished by an endothermic transition at 180 °C in the DTA curve, corresponds to the loss of water molecules weakly bound to the material. The second weight loss, taking place between 230 and 600 °C, accomplished by a broad exothermic peak at 400 °C in the DTA curve, corresponds to the pyrolysis and oxidation of residual alkyl halide groups, followed by decomposition of the complex. When compared with Fig. 4A, it can be seen that decomposition of the complex occurred between 300 and 600 °C for both materials, showing that the thermal stability of Mn(salen) was not modified upon its incorporation into the alumina network.

3.2. Catalytic results

Mn(III)salen complexes have been reported by Jacobsen and co-workers [2–6], Katsuki and co-workers [7–11], and other researchers [29–31] as being versatile catalysts for the oxidation of hydrocarbons in the presence of several oxidants. However, one of the major drawbacks to the use of these homogeneous complexes as catalysts is their irreversible deactivation via formation of μ-oxo and μ-peroxo dimers [12,32,33]. Products and
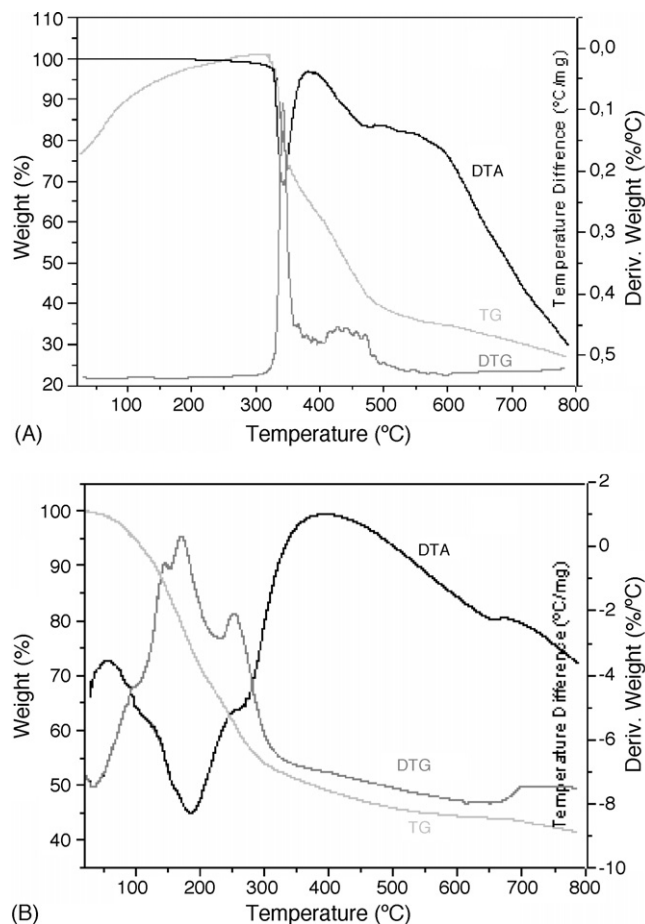

Fig. 4. (A) TGA–DTA–DSC curves of the Jacobsen catalyst, Mn(salen). Heating rate: 20 °C/min. (B) TGA–DTA–DSC curves of the alumina containing Jacobsen catalyst, Mn(salen)-NHG. Heating rate: 20 °C/min.

catalyst separation also remains troublesome with these homogeneous systems [34].

The formation of bulky dimeric species is sterically hindered when monomeric complexes are immobilized on solid supports,

Table 2
Results obtained for cyclooctene oxidations by several oxidants catalyzed by Mn(salen) or Mn(salen)-NHG

Entry	Oxidant	Catalyst	Product (cyclooctene oxide)	
			TOF[a] (h^{-1})	Yield[b] (%)
1	m-CPBA	Mn(salen)	35	25
2		Mn(salen)-NHG	103	79
3	t-BuOOH	Mn(salen)	nd	nd
4		Mn(salen)-NHG	3	2
5	PhIO	Mn(salen)	16	13
6		Mn(salen)-NHG	19	16
7	IBDA	Mn(salen)	nd	nd
8		Mn(salen)-NHG	9	8
9	H_2O_2 70%	Mn(salen)	29	23
10		Mn(salen)-NHG	86	70

[a] Turnover frequency: mol of product/mol of catalyst per time.
[b] % yield based on added oxidant after 8 h; nd: not detected (<1); reactions using H_2O_2 30% as oxidant: nd.

Table 3
Results obtained for styrene oxidations by several oxidants catalyzed by Mn(salen) or Mn(salen)-NHG

Entry	Oxidant	Catalyst	Products					
			Benzaldehyde		Styrene oxide		Phenyl[a]	
			TOF[b] (h^{-1})	Yield[c] (%)	TOF (h^{-1})	Yield (%)	TOF (h^{-1})	Yield (%)
1	m-CPBA	Mn(salen)	nd	nd	26	12	nd	nd
2		Mn(salen)-NHG	11	8	87	68	nd	nd
3	t-BuOOH	Mn(salen)	21	10	nd	nd	nd	nd
4		Mn(salen)-NHG	23	11	nd	nd	nd	nd
5[d]		Mn(salen)	9	6	7	3	nd	nd
6[d]		Mn(salen)-NHG	6	4	13	6	nd	nd
7[e]	PhIO	Mn(salen)-NHG	nd	nd	22	17	23	16
8[e]	IBDA	Mn(salen)-NHG	nd	nd	23	16	40	28
9	H_2O_2 70%	Mn(salen)	nd	nd	9	4	nd	nd
10		Mn(salen)-NHG	nd	nd	71	55	nd	nd

[a] Phenylacetaldehyde.
[b] Turnover frequency: mol of product/mol of catalyst per time.
[c] % yield based on oxidant added after 8 h.
[d] In argon atmosphere; nd: not detected (<1).
[e] Reactions in homogeneous solution: nd; reactions using H_2O_2 30% as oxidant: nd.

such as zeolites, poly(dimethylsiloxane) membranes, and alumina matrix, explaining the recent interest in these materials as supports for Mn(salen) catalysts [29,35–39]. These heterogeneous systems offer improved lifetime, enable easy catalyst recovery from the reaction mixture, and simplify product purification.

The catalytic activity of the studied system was investigated using (Z)-cyclooctene, styrene, and cyclohexane as substrates. The catalytic oxidation results were measured in terms of turnover frequencies and percentage yields.

Catalytic results in Tables 2 and 3 show that the Mn(salen)-NHG is a more efficient catalyst for the epoxidation of (Z)-cyclooctene and styrene than the corresponding homogeneous system with all the studied oxidants, except for H_2O_2 30%. The higher efficiency of the supported catalyst is due to the role of the support in guiding the reactants to the active catalytic site, besides avoiding the catalyst destruction or formation of dimeric complexes that generate inactive species.

In order to investigate whether catalyst leaching could occur during the oxidation reactions, the supernatant was filtered at the end of reaction and allowed to react further in the same conditions. No additional epoxide was produced from the oxidation of cyclooctene indicating that the catalytic activity of this supported material is truly heterogeneous in nature and this complex was not leached from the matrix.

Product yields are highly dependent on the nature of the oxidant (Tables 2 and 3). The best oxidant for the Mn(salen)-NHG catalyzed epoxidation of (Z)-cyclooctene and styrene is m-CPBA, in both homogeneous and heterogeneous systems (Tables 2 and 3, entries 1 and 2). This oxidant is also the best when compared with t-BOOH in the case of oxidations catalyzed by other complexes such as $Cl_{16}PcFe$,[1] an iron phtalo-

cyanine [40]. When peroxide oxidants are used, two mechanisms for oxygen activation are possible: one involves the homolytic cleavage of the O–O peroxide bond, with $RO^{\bullet}$ as the active species, resulting in low selectivity; the other involves the heterolytic cleavage of the O–O bond, with formation of the $Mn^V(O)$salen species, responsible for the epoxidation [41]. In the reaction with m-CPBA, the formation of cyclooctene oxide and styrene oxide as main products indicates that the $Mn^V(O)$salen species is the active oxidant, generated through heterolysis of the peroxide, which is favored by the presence of the electron-withdrawing substituents on the phenyl group of this oxidant.

In the reactions with t-BuOOH, the production of epoxide was not favored and benzaldehyde was the main product (Table 3, entries 3 and 4). The formation of such product is attributed to radicalar reactions [42]. Alkyl-hydroperoxides (alkyl donor group) tend to undergo homolytic cleavage of the peroxide O–O bond upon coordination to the salen central manganese. This results in the formation of the poorly reactive intermediate, $Mn^V(OH)$salen, responsible for the low epoxide yields and the formation of $RO^{\bullet}$ radicals [43]. The latter species initiate radicalar reactions that are continued by the oxygen present in the solution, leading to the formation of benzaldehyde. When the reaction is carried out under argon, the benzaldehyde yield is significantly reduced, and the selectivity toward styrene oxide is increased (Table 3, entries 3–6). These results give evidence that alkyl radicals are formed in the reaction and they could be trapped by O_2.

PhIO has been extensively used as oxidant in oxidation reactions catalyzed by metalloporphyrin and similar systems [44]. However, lower yields (overall 32%, Table 3, entry 7) were obtained for the oxidation of alkenes in this study when compared with m-CPBA. This is probably due to the difficulty of this poorly soluble oxidant in reaching the catalyst inside the matrix. In the presence of H_2O, IBDA produces PhIO in situ, which in

[1] $Cl_{16}PcFe$: iron polychlorophthalocyanine.
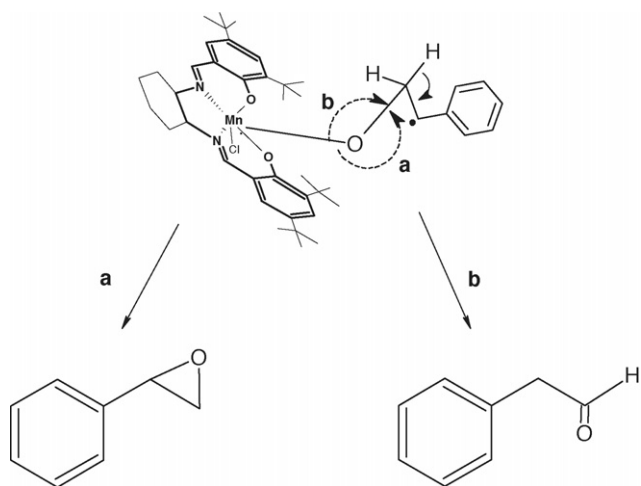
Scheme 1. Possible reaction paths for the oxygen transfer from the Mn(salen) intermediate to styrene.

turn reacts with the catalyst leading to alkene epoxidation [45]. However, the generation of PhIO *in situ* is slow and depends on the presence of H_2O in the reaction environment [46].

Formation of relatively large quantities of phenylacetaldehyde in the oxidation of styrene catalyzed by Mn(salen)-NHG using PhIO and IBDA (Table 3, entries 7 and 8) was observed. Control experiments using styrene oxide as substrate under the same reaction conditions showed that phenylacetaldehyde is not generated from the rearrangement of styrene oxide. Therefore, the formation of phenylacetaldehyde competes with the formation of epoxide. In fact, Groves [47] has proposed a mechanism that accounts for the parallel formation of phenylacetaldehyde and styrene oxide in the system involving metalloporphyrins, and Scheme 1 shows an adapted scheme to explain the results obtained in this work. In this scheme, an asymmetric transition that generates the epoxide (path a), or the phenylacetaldehyde by rearrangement (path b), can be observed. The latter is analogous to the well-established NIH rearrangement [47]. Therefore, the formation of phenylacetaldehyde is related to the reactivity of the intermediate species (activated complex—Scheme 1) in a way that, the lower its reactivity, the longer its lifetime and thus, the higher the probability that hydrogen rearrangement may occur, leading to the formation of phenylacetaldehyde (path b). In this way, because of the low solubility of PhIO in the reaction medium, as well as the slow generation of PhIO *in situ* in the case of IBDA, the reaction is slow enough to favour the rearrangement leading to phenylacetaldehyde yields of about 16 and 28% when PhIO and IBDA are used, respectively (Table 3, entries 7 and 8).

We observed that Mn(salen)-NHG can efficiently catalyze the oxidation of cyclooctene and styrene using aqueous 70 wt.% H_2O_2 as oxygen donor (yields of 70% and 55%, respectively, Table 2, entry 10 and Table 3, entry 10), although aqueous 30 wt.% H_2O_2 is not an active oxidant in this system. The larger amount of water in more diluted H_2O_2 probably makes the alumina surface more hydrophilic, with formation of a dense water layer on the surface, thus hindering the olefin approach to the active site of the catalyst and the subsequent diffusion of the

products. Schuchardt et al. [48] have shown that large amounts of water (aqueous 30 wt.% hydrogen peroxide) strongly reduce the epoxidation reaction rate when boehmite and γ-alumina were used as catalyst, an observation that is in agreement with the results of this study.

Cyclohexane oxidation is an important bulk process for the production of polyamide fibers and plastics. Cyclohexanone is an intermediate in the production of adipic acid, which is further used in the production of the polymers Nylon-6 and Nylon-6,6. More than 10^6 tonnes of cyclohexanone and cyclohexanol are produced worldwide per year using the DuPont process [49–52]. The conversion of cyclohexane into these products is kept under 5% to avoid their over-oxidation, and consequently the unreacted cyclohexane needs to be extracted and recycled. This is one reason why increasing the efficiency and selectivity of hydrocarbon transformations has been the goal of both academic and industrial research efforts [49–52].

In our present study, neither cyclohexanol nor cyclohexanone were found in the oxidation of cyclohexane by different oxidants carried out in the absence of Mn(salen).

Mn(salen)-NHG is a good catalyst for cyclohexane oxidation and it is highly selective (95%) for cyclohexanone (Table 4), despite the fact that the neat complex produces a mixture of cyclohexanol and cyclohexanone in a ratio lying between 1.5 and 2.5, when peroxides (m-CPBA, t-BuOOH and H_2O_2 70% Table 4, entries 1, 3, and 9) are used as oxidant. The selectivity for cyclohexanone observed for Mn(salen)-NHG can be explained by considering the over-oxidation of cyclohexanol under the reaction conditions. Mechanistic studies using a similar system involving metalloporphyrin-zeolites showed that alcohol is selectively oxidized to ketone inside the pores of the matrix [53]. The alumina surface exhibits higher affinity for the more polar oxidation product (cyclohexanol), promoting its over-oxidation. This was proven when the reaction was monitored at short intervals. Almost only cyclohexanol was observed during the first 90 min of reaction. After about 2 h, the alcohol/ketone ratio decreased, thus indicating conversion of alcohol to the ketone (Fig. 5). In addition, control experiments using cyclohexanol as substrate in the same conditions showed that cyclohexanone
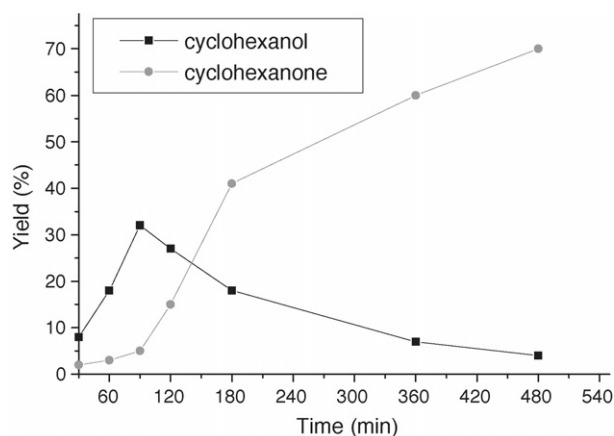

Fig. 5. Cyclohexanone and cyclohexanol yields as a function of reaction time, obtained in the catalytic reaction of cyclohexane.

Table 4
Results obtained for cyclohexane oxidations by several oxidants catalyzed by Mn(salen) or Mn(salen)-NHG

Entry	Oxidant	Catalyst	Products			
			Cyclohexanone		Cyclohexanol	
			TOF[a] (h^{-1})	Yield[b] (%)	TOF (h^{-1})	Yield (%)
1	m-	Mn(salen)	5	4	11	9
2	CPBA	Mn(salen)-NHG	210	70	5	4
3		Mn(salen)	6	2	6	5
4	TBHP	Mn(salen)-NHG	59	46	3	2
5[c]	PhIO	Mn(salen)-NHG	56	44	11	9
6[c]	IBDA	Mn(salen)-NHG	52	41	6	5
7	H_2O_2	Mn(salen)	5	4	7	6
8	70%	Mn(salen)-NHG	19	15	7	6

[a] Turnover frequency: mol of product/mol of catalyst per time.
[b] % yield based on oxidant added after 8 h; nd: not detected (<1).
[c] Reactions in homogeneous solution: nd; reactions using H_2O_2 30% as oxidant: nd.

was formed from the oxidation of cyclohexanol in the presence of Mn(salen)-NHG. In conclusion, the ketone formation should not compete with alcohol formation as observed for the homogeneous catalyst, for which the cyclohexanone yield was reduced to half of its value (ol: one ratio increased to 4.31) when reactions were carried out under argon.

It has been reported that oxo-manganese(V) species is the reactive intermediate for alkane hydroxylation catalyzed by the salen complex, using sodium periodate as the oxygen source [54]. The hydroxylation mechanism of the neat Mn(salen) complex can be compared to the oxygen rebound mechanism of Mn-porphyrin. In this mechanism, the high-valent $Mn^V(O)$ species abstracts a hydrogen atom from the alkane, generating a short-lived alkyl radical and a $Mn^{IV}(OH)$ complex in a solvent cage. Rapid hydroxyl transfer from this complex to the alkyl radical produces the alcohol. Ketone production can be explained by escape of the alkyl radicals from the solvent cage, which react with O_2 to produce peroxyl radicals [55–58]. The latter radicals react with cyclohexane to furnish cyclohexanone. However, in the currently studied system, the ketone is generated from alcohol over-oxidation.

3.3. Catalyst recycling

For as long as catalysts have been used to perform reactions much effort has been devoted not only to the development of superior catalysts but also to finding ways to enable their repeated use or their use in continuously operated reactors.

In order to investigate this possibility for Mn(salen)-NHG, the catalyst was separated from the reaction mixture by filtration after the reaction, washed with CH_2Cl_2, dried at room temperature, and used again in a fresh reaction. The catalyst was recycled five times for cyclooctene and styrene epoxidations and for cyclohexane oxidation using the best oxidant, m-CPBA. No substantial loss in the catalytic activity of the immobilized catalyst was observed when compared with that of fresh sample,

as shown in Fig. 6, thus showing that recycling is possible for Mn(salen)-NHG.

3.4. Stability of the Mn(salen)-NHG catalyst in repeated oxidations

In order to investigate the catalyst stability in the Mn(salen)-NHG catalyzed oxidation of cyclooctene and styrene, the products were monitored for six additions of oxidant (PhIO, IBDA, m-CPBA, H_2O_2 70%) (each one with catalyst:oxidant, 1:1000) added at 24-h intervals (Figs. 7 and 8).

m-CPBA and hydrogen peroxide (70%) were the best oxidants for repeated oxidations, being the epoxide yields almost constant for cyclooctene oxide (96%, 733 TOF total) and styrene oxide (91%, 714 TOF total), Figs. 7 and 8.

Epoxide yield decreased slightly after the third addition when PhIO and IBDA were used as oxidants. From these results, it can be assumed that Mn(salen)-NHG can be deactivated possibly by
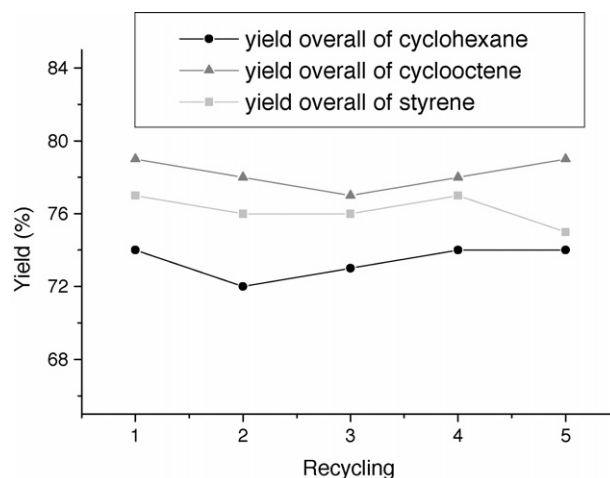

Fig. 6. Recycling data for cyclooctene, styrene, and cyclohexane oxidations using the immobilized catalyst Mn(salen)-NHG and m-CPBA as oxidant.
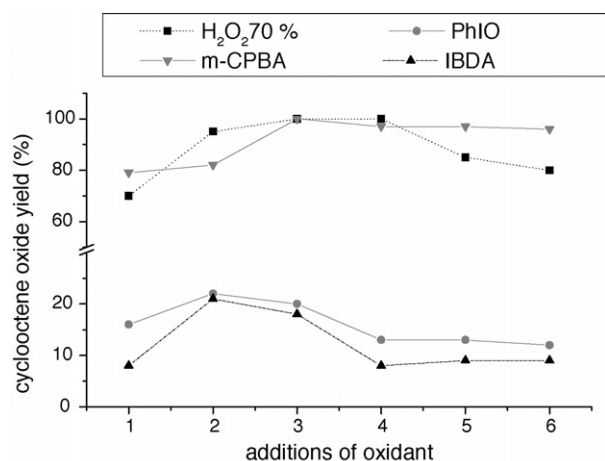
Fig. 7. Cyclooctene epoxidation with repeated additions of oxidant, catalyzed by Mn(salen)-NHG in acetonitrile.
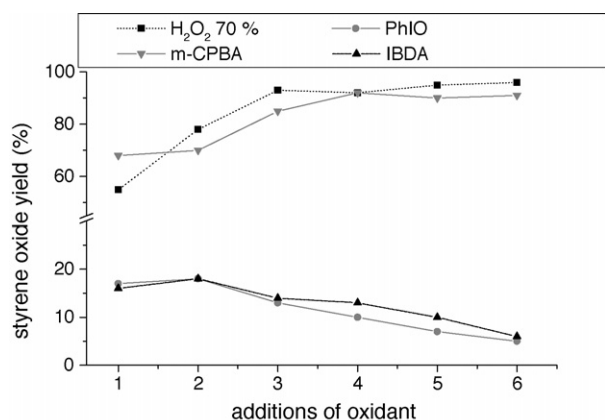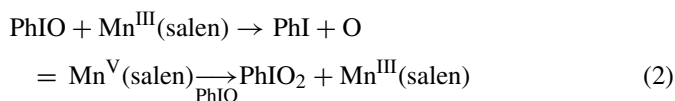

Fig. 8. Styrene epoxidation with repeated additions of oxidant, catalyzed by Mn(salen)-NHG in acetonitrile.

precipitation of iodoxybenzene, originated from the catalyzed disproportionation of iodosylbenzene [reaction (2)] on the catalyst surface [59]:

$$PhIO + Mn^{III}(salen) \rightarrow PhI + O$$

$$= Mn^{V}(salen) \xrightarrow[PhIO]{} PhIO_2 + Mn^{III}(salen) \qquad (2)$$

After the sixth addition of oxidant (PhIO and IBDA), the Mn(salen)-NHG was recovered by filtration, washed with DCM, dried, and reused in a fresh reaction. This treatment restored the activity of the catalyst, leading to results similar to those obtained in the first reaction.

4. Conclusion

A hybrid material containing the Mn(salen) complex entrapped in alumina matrix has been successfully prepared. The Mn(salen)-NHG material catalyzes (Z)-cyclooctene, styrene, and cyclohexane oxidations by different oxidants (PhIO, IBDA, m-CPBA, t-BOOH, H_2O_2) leading to better product yields if compared with the catalyst in homogeneous solution. Moreover, this new catalyst did not leach from the support and was reused

many times, reaching high turnover frequencies. These results show the catalytic potential of this system and also emphasize the role of the non-hydrolytic alumina matrix in preventing the chemical degradation of the Mn(salen) and providing enhanced stability to the catalyst. The further development of a reactor for this promising system that will be able to carry out larger scale oxidations are our challenges for the near future.

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