The catalytic activity of poly(siloxane)-supported metalloporphyrins in olefin oxidation reactions: the effect of the support on the catalytic activity and selectivity

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Abstract

Supported tetra(-4-pyridyl)porphyrinato-manganese(III) [Mn^{III}(TPyP)]$^+$ and -tin(IV) [Sn^{IV}(TPyP)]$^{2+}$ have been prepared. The solid support was iodonated poly(siloxane) surface prepared by condensation reactions of $(EtO)_4Si$ with $(MeO)_3Si(CH_2)_3I$. The supported metalloporphyrins were employed as catalysts for the oxidation reactions of 1-octene and of cyclohexene. $NaBH_4$ was used to reduce [Mn^{III}(TPyP)]$^+$ and [Sn^{IV}(TPyP)]$^{2+}$ back to their catalytically active Mn^{II} and Sn^{II} forms, respectively. Contrary to their homogeneous counterparts, both of the supported metalloporphyrins catalysed the cyclohexene oxidation reaction to yield only 2-cyclohexen-1-one with no other products over a reaction time of 10 h. In addition to cyclohexene oxidation, the supported [Mn^{III}(TPyP)]$^+$ catalysed 1-octene oxidation as well, whereas the supported [Sn^{IV}(TPyP)]$^{2+}$ was inactive for the oxidation of 1-octene.

Keywords: Cyclohexene; Poly(siloxane)-supported catalysts; Manganese; Metalloporphyrins; Oxidation; Siloxane; Supported catalysts; Tin

1. Introduction

Metalloporphyrin compounds MP homogeneously catalyse the aerobic oxidation reactions of olefins [15], phenols [6,7], indoles [8] and other organic substrates [9] in the presence of $NaBH_4$. Examples of known metalloporphyrin catalysts are those of Co, Mn, Zn, Fe and others.
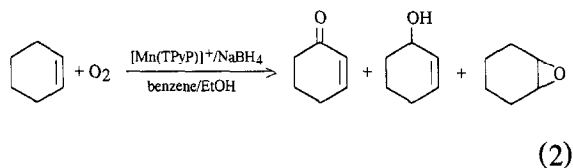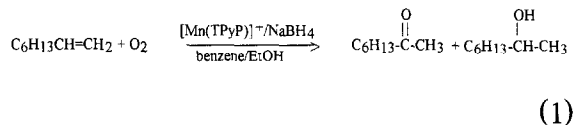
Tetra(-4-pyridyl)porphyrinatomanganese(III) [Mn(TPP)]$^+$ homogeneously catalyses the oxi-

dation of olefins, eg. 1-pentene, 1-octene and cyclohexene, under mild conditions by atmospheric oxygen in the presence of $NaBH_4$ in different solvents [10,11]. Porphyrinatotin(IV) complexes have not to our knowledge been widely used as catalysts for such reactions.

Despite the fact that metalloporphyrins homogeneously catalyse the oxidation reactions of olefins, the homogeneous catalytic systems suffer two shortcomings. Firstly, the catalyst is difficult to isolate. Secondly, the homogeneous catalytic systems did not show high selectivity. Two or more reaction products appeared during

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the $[Mn(TPyP)]^+$-catalysed aerobic oxidation of cyclohexene [5], cyclooctene [1], and other terminal olefins [1], (Eqs. (1) and (2))

$$C_6H_{13}CH=CH_2 + O_2 \xrightarrow[\text{benzene/EtOH}]{[Mn(TPyP)]^+/NaBH_4} C_6H_{13}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + C_6H_{13}\text{-}\overset{OH}{\overset{|}{CH}}\text{-}CH_3$$

(1)

(2)

Scheme 1.

In our search for new classes of olefin oxidation reaction catalysts, we have been trying to develop industrially valuable catalytic systems. Among the features we look for are (1) ease of separation of the catalyst after use, (2) high catalytic selectivity toward the ketonic product and (3) high catalytic activity. The first feature can be achieved simply by supporting the catalytic species onto insoluble solid matrices. The supporting technique can be done either by adsorption onto the surface or by primary chemical bond attachment. Both of these techniques are known [12]. Metalloporphyrin catalysts adsorbed onto supports such as glassy carbon and ion exchange resins are known [13]. Metalloporphyrins (MP) supported onto metal electrodes have been frequently employed as electro- or photo-catalysts [13–19] for a variety of redox, disproportionation and decomposition reactions.

Covalent attachment of chemically regenerated metalloporphyrin catalysts onto insoluble solids has been reported, but to a lesser extent [20]. Pretreated organic polymers have been used as supports for chemically regenerated porphyrinatomanganese(III) catalysts in cholesterol [21] and other olefin [3] oxidations. In our preceding papers [22–24] we described the preparation
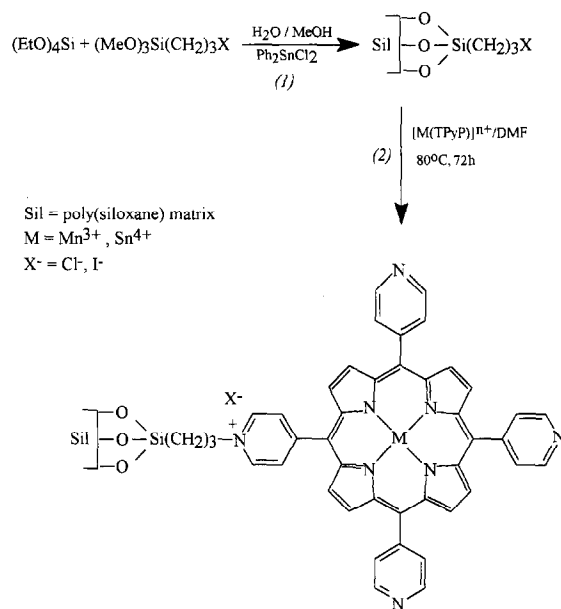
and characterisation of chlorinated poly(siloxane)-supported $[Mn(TPyP)]^+$ complex together with its catalytic activity in thermal oxidation of olefins by atmospheric oxygen in the presence of $NaBH_4$ under mild conditions.

This communication is entirely devoted to show the effect of chemical attachment of metalloporphyrins to poly(siloxane) surfaces on their catalytic activity and selectivity in olefin thermal aerobic oxidation reactions. Two metalloporphyrin complexes $[Mn\{TPyP\}]^+$ and $[Sn(TPyP)]^{2+}$ have been used here. The supported $[Sn(TPyP)]^{2+}$ is described for the first time. The anchoring of the MP was achieved by quaternising the complex pyridyl group with the surface C–I groups, as shown in Scheme 1. The iodonated surfaces were chosen here as alternatives to chlorinated surfaces. This is because the C–I groups react with pyridyl groups faster than C–Cl groups do [25–27].

Comparisons of catalytic activity and selectivity of supported metalloporphyrins with their homogeneous counterparts, in olefin aerobic oxidation, are presented here.

2. Experimental

The organic solvents, the cyclohexene and the 1-octene were purchased from Aldrich Co. Ltd and dried prior to use by standard methods [28]. $(EtO)_4SiH$, $NaBH_4$, $(MeO)_3Si(CH_2)_3Cl$, 5,10,15,20-tetra(-4-pyridyl)-21H,23H-porphin and other reactants were purchased from Aldrich in a reagent grade pure form.

IR spectra were measured, on a Pye Unicam SP3-200 dispersion spectrophotometer, or on a Shimadzu FTIR-8201PC Fourier transform spectrophotometer, using thin layers between NaCl discs. Electronic absorption spectra were measured on a Pye Unicam SP8-100 UV/visible spectrophotometer using quartz cells. Gas chromatographic analyses were conducted using a Pye Unicam gas chromatograph equipped with a hydrogen flame detector and an E-30 type glass column (2.5 m long and 6 mm in diameter). The detector temperature was set at 270°C, and the oven temperature was 150°C.

The metalloporphyrins $[Mn(TPyP)]^+$ and $[Sn(TPyP)]^{2+}$ were prepared as reported earlier [23] using the DMF method described by Adler et al. [29,30]. The solid support was prepared as reported earlier [31] with one modification. Instead of using $(MeO)_3Si(CH_2)_3Cl$, $(MeO)_3Si(CH_2)_3I$ was used. The preparation of $(MeO)_3Si(CH_2)_3I$ was achieved using the Finkelstein reaction [28], as follows: NaI (20.0 g, 0.133 mol) was dissolved in minimum acetone followed by addition of $(MeO)_3Si(CH_2)_3Cl$ (19.26 g, 0.097 mol) at room temperature. The reaction took place and the NaCl white solid precipitated out of the reaction solution, since NaCl is insoluble in acetone. The resulting $NaCl_{(s)}$ was separated by filtration, dried and weighed. The amount of $NaCl_{(s)}$ was stoichiometric with that of $(MeO)_3Si(CH_2)_3Cl$ used, which indicates complete iodization of the reactant. The volume of acetone was then reduced to half, and H_2O (50 ml) was added while shaking. The organic layer, with the ligand $(MeO)_3Si(CH_2)_3I$, was separated by a separatory funnel to eliminate traces of aqueous NaCl.

Washing with H_2O was repeated several times to fully eliminate NaCl. The organic layer was then dried by a drying agent. IR spectra measured for the organic layer confirmed the absence of the C–Cl bands in the range 730–720 cm^{-1} [32,33]. The product was then separated by distillation under reduced pressure. The isolated product did not show any IR band at 729 cm^{-1} which was observed for the reactant $(MeO)_3Si(CH_2)_3Cl$. The iodization was also chemically confirmed. Addition of $AgNO_3$(aq), to the isolated reaction product, produced a yellow precipitate, indicating the presence of the iodide. The conversion of $(MeO)_3Si(CH_2)_3Cl$ into $(MeO)_3Si(CH_2)_3I$ has been also described elsewhere [43] and complete conversion into the iodized form is known by results of elemental analysis.

$(MeO)_3Si(CH_2)_3I$ was allowed to react with $(EtO)_4Si$ to produce the solid support surface, following the methods described by Khatib and Parish [31] with some modifications. $(MeO)_3Si(CH_2)_3I$ (11.2 g, 0.04 mol) was refluxed with $(EtO)_4Si$ (16.0 g, 0.08 mol) in the presence of catalyst $(CH_3CO_2)_2Sn[(CH_2)_2CH_3]_2$ (1.1 g, 0.032 mol) and H_2O (4.8 g, 0.267 mol). The reactant molar ratio of $(EtO)_4Si/(MeO)_3Si(CH_2)_3I$ (2:1) was used to obtain a high degree of cross-linking in the resulting solid matrix, as reported earlier [31,43–45]. The solid support contains only $-Si(CH_2)_3I$ not $-Si(CH_2)_3Cl$ surface groups as described earlier [31,43–45].

The metalloporphyrins $[Mn(TPyP)]^+$ and $[Sn(TPyP)]^{2+}$ were anchored to the iodonated poly(siloxane) by allowing them to react at 70°C in DMF for 20 h. Details of preparations and solid state analyses of the supported metalloporphyrins were reported earlier [22,23]. UV/visible spectra measured for the remaining unreacted metalloporphyrin solutions showed no detectable demetallation. To avoid demetallation of the metalloporphyrin refluxing conditions were avoided.

The metalloporphyrin uptake onto the support was measured spectrophotometrically.

Quantitative and qualitative spectral analyses for the supported metalloporphyrins were described in our earlier reports [22–24]. The degree of quaternization (DQ, mole of free halide produced per mole of supported metalloporphyrin) was measured by ion exchange chromatography as described elsewhere [23]. Due to steric effects the value of DQ did not exceed 2.0.

Different batches were prepared for both $[Sn(TPyP)]^{2+}$ and $[Mn(TPyP)]^{+}$ supported species. The metalloporphyrin uptake was not reproducible among different preparations.

2.1. Catalysis experiments

The catalysis experiments were conducted, as reported earlier [24], in a 250 ml round bottom flask equipped with a magnetic stirring system, a thermostated water bath and a cooled condenser open to air. A typical reaction run was conducted as follows: The cleaned reactor was thermostated at the desired temperature, and charged with the supported catalyst, the $NaBH_4$ reducing agent (excess 1.0 g, 26.0 mmol), solvent (enough to make total volume 10.0 ml each time) and olefin, with stirring. Reaction timing was started from the moment the olefin was injected. Aliquots, (0.2 ml), were syringed out from the reaction mixture at different times, immediately sealed, chilled, decanted and analysed as described in earlier reports [11].

For comparison purposes, catalytic reaction runs were conducted using catalyst samples taken from same batch. Arbitrarily, batches with 3.0×10^{-4} and 1.0×10^{-5} (mol/g support) uptakes for $[Sn(TPyP)]^{2+}$ and $[Mn(TPyP)]^{+}$ respectively were employed in the catalytic experiments, unless otherwise stated.

3. Results and discussion

Addition of cyclohexene to air-exposed mixtures of poly(siloxane)-supported $[Sn(TPyP)]^{2+}$ or $[Mn(TPyP)]^{+}$ in toluene with or without $NaBH_4$ resulted in the exclusive production of 2-cyclohexen-1-one with no other detectable reaction products over a period of 10 h or longer. The amount of product 2-cyclohexen-1-one was stoichiometric with the amount of reacted cyclohexene. The production of 2-cyclohexen-1-one was confirmed by GC and IR spectral analyses. The IR spectrum, with a band at 1645 cm^{-1}, measured for the reaction product, matched that measured for authentic, commercial reagent-grade 2-cyclohexen-1-one. The IR band is also in agreement with literature [32,34]. GC retention time for the reaction product also matched that of the authentic 2-cyclohexen-1-one. Control experiments were carried out in the absence of the metalloporphyrins, with and without $NaBH_4$, and no reaction was observed. Metalloporphyrin-free poly(siloxane) surfaces did not cause any chemical changes either. This indicates that the oxidation reaction described here is exclusively caused by the supported metalloporphyrins.

The supported metalloporphyrins showed an important feature. The aerobic oxidation reactions of cyclohexene, catalysed by the supported metalloporphyrins, were faster than those catalysed by their homogeneous counterparts. Table 1 shows that the supported $[Sn(TPyP)]^{2+}$ catalyst, in cyclohexene oxidation, is much more effective than that of the homogeneous counterpart. Values of turnover frequency (TF) of up to 300 h^{-1} were observed for the supported $[Sn(TPyP)]^{2+}$, compared to ≈ 1 h^{-1} for the homogeneous system. Similarly, the supported $[Mn(TPyP)]^{+}$ catalyst, with TF values up to 350 h^{-1}, was more effective than its homogeneous counterpart, Table 1. These results indicate that the support enhances the catalytic activity of the metalloporphyrin ions. The enhancement of catalytic activity of supported compounds is known for metalloporphyrins [21] and other classes of complexes [38].

Homogeneous and supported $[Sn(TPyP)]^{2+}$ did not catalyse the oxidation reaction of 1-octene under conditions similar to those used for cyclohexene, Table 1. $[Mn(TPyP)]^{+}$, in both its

Table 1
Effect of support on the catalytic activity [a] of $[Sn(TPyP)]^{2+}$ and $[Mn(TPyP)]^+$ in the aerobic oxidation reactions of olefins

Entry	Catalyst	Catalyst concentration [b] $(M) \times 10^4$	Olefin	Time (h)	Conversion [c] (%)	TF [c] (h^{-1})
1 [d]	$[Sn(TPyP)]^{2+}$	600	cyclohexene	5	1	< 1
2 [e]	$[Sn(TPyP)]^{2+}$	600	cyclohexene	5	< 1	≈ 0
3 [d]	supported $[Sn(TPyP)]^{2+}$	106	cyclohexene	5	15	300
4 [e]	supported $[Sn(TPyP)]^{2+}$	106	cyclohexene	5	10	110
5 [d]	$[Mn(TPyP)]^+$	600	cyclohexene	40	30	70
6 [e]	$[Mn(TPyP)]^+$	600	cyclohexene	40	5	< 1
7 [d]	supported $[Mn(TPyP)]^+$	6	cyclohexene	40	85	350
8 [e]	supported $[Mn(TPyP)]^+$	6	cyclohexene	40	2	0
9 [d]	$[Sn(TPyP)]^{2+}$	600	1-octene	5	0	0
10 [d]	supported $[Sn(TPyP)]^{2+}$	106	1-octene	5	0	0
11 [d]	$[Mn(TPyP)]^+$	600	1-octene	40	5	35
12 [d]	supported $[Mn(TPyP)]^+$	6	1-octene	40	25	100

[a] All reactions were conducted at 30°C in toluene (9.0 ml), using cyclohexene (1.0 ml, 0.98 M).
[b] Moles of MP per liter reaction solution.
[c] Based on olefin oxidation to ketone product.
[d] With excess $NaBH_4$ (1.0 g, 0.0264 mol).
[e] Without $NaBH_4$.

homogeneous and supported versions, catalysed the oxidation of 1-octene to octan-2-one. As in cyclohexene oxidation, supported $[Mn(TPyP)]^+$ showed higher catalytic activity than its homogeneous counterpart, as appears from entries (11) and (12), Table 1. Since homogeneous and supported $[Sn(TPyP)]^{2+}$ complexes failed to catalyse the 1-octene oxidation, the activities of these two types of catalysts could not be compared for such reaction. Therefore, the present comparative study is restricted to only cyclohexene oxidation, unless otherwise stated.

The selectivity of the supported metalloporphyrins to produce 2-cyclohexen-1-one is an important feature of this class of catalysts. Re-

sults showing the effect of the support on the product distributions are listed in Table 2. Within certain periods of reaction time, the sole oxidation product of cyclohexene was 2-cyclohexen-1-one in cases of supported $[Sn(TPyP)]^{2+}$ and $[Mn(TPyP)]^+$, entries (2) and (4). On the other hand, the homogeneous catalyst counterparts produced mixtures of products as appears in entries (1) and (3). With homogeneous metalloporphyrin catalysis of cyclohexene aerobic oxidation, different reaction products are known to appear concurrently [1,3,6,10,35–37]. Therefore, the selectivity of the supported metalloporphyrins to produce only one product, over a period of reaction time, is a good feature.

Table 2
Comparison of catalyst activities of supported $[Sn(TPyP)]^{2+}$ and $[Mn(TPyP)]^+$ with their homogeneous counterparts in the aerobic oxidation of cyclohexene [a] into 2-cyclohexene-1-one and cyclohexen-1-ol

Entry	Catalyst	Catalyst concentration [b] $(M) \times 10^4$	TF(2-cyclohexen-1-one)/TF(cyclohexen-1-ol) [c]	
1	$[Sn(TPyP)]^{2+}$	600	5/3 (5 h)	2.5/7.5 (10 h)
2	supported $[Sn(TPyP)]^{2+}$	106	300/0 (5 h)	210/90 (10 h)
3	$[Mn(TPyP)]^+$	600	70/30 (5 h)	560/60 (60 h)
4	supported $[Mn(TPyP)]^+$	6	350/0 (40 h)	220/100 (60 h)

[a] All reactions were conducted at 30°C in toluene (9.0 ml) using cyclohexene (1.0 ml, 0.98 M) and excess $NaBH_4$ (1.0 g, 0.026 mol).
[b] Moles $[M(TPyP)]^{n+}$ per liter reaction solution.
[c] Measured after reaction times shown in brackets below.

Table 3
Effect of recovery on the catalytic activity [a] of supported metalloporphyrins in cyclohexene oxidation

Entry	Catalyst	Catalyst concentration [b] (M) $\times 10^4$	Time (h)	Conversion [c] (%)	TF [c] (h^{-1})
1	fresh [Sn(TPyP)]$^{2+}$	106	5	15	300
2	recovered [Sn(TPyP)]$^{2+}$	106	5	< 1	20
3	fresh [Mn(TPyP)]$^+$	6	40	85	350
4	recovered [Mn(TPyP)]$^+$	6	40	4	4

[a] All reactions were conducted at 30°C in toluene (9 ml) using NaBH$_4$ (1.0 g, 0.026 mol) and cyclohexene (1.0 ml, 0.98 M).
[b] Moles [M(TPyP)]$^{n+}$ per liter reaction solution.
[c] Based on cyclohexene oxidation to 2-cyclohexen-1-one.

The supported [Mn(TPyP)]$^+$ and [Sn(TPyP)]$^{2+}$ species had comparable catalytic activities, in the cyclohexene oxidation reaction, as appears from their values of TF when keeping other reaction parameters the same, entries (2) and (4), Table 2. In this regard, though, there is no preference in using one of these two systems or the other. However, the supported [Mn(TPyP)]$^+$ has one advantage over the supported [Sn(TPy)]$^{2+}$ in terms of the catalytic selectivity. In case of the former, the cyclohexene oxidation reaction was selective only to 2-cyclohexen-1-one over prolonged times, ca. 40 h. In the case of the supported [Sn(TPyP)]$^{2+}$, the catalytic reaction mixture was selective to 2-cyclohexen-1-one over a relatively shorter period of time, ca. 5 h, after which the product concentration started to decrease. Hydrogena-

tion of the reaction product to 2-cyclohexen-1-ol was the major route to the consumption of the 2-cyclohexen-1-one product. This is in accord with other reports, where the ketone products were reduced to corresponding alcohols by the dissolved NaBH$_4$ [1,5].

The effect of NaBH$_4$ on the aerobic oxidation of cyclohexene was investigated. The supported metalloporphyrin-catalysed reaction was faster when conducted in the presence of NaBH$_4$, Table 1. This is attributed to the ability of NaBH$_4$ to convert the metal central ions Sn^{IV} and Mn^{III} back to their lower oxidation states Sn^{II} and Mn^{II}, respectively [1,6,10,37]. It has been proposed that metalloporphyrins activate dioxygen O$_2$ when the central metal ions exist in their lower oxidation state (2 +), and that this activation is necessary for the oxidising

Table 4
Effect of temperature on the catalytic activity of supported metalloporphyrins in cyclohexene oxidation to 2-cyclohexen-1-one

Entry	Catalyst	Reaction time (h)	Temperature (°C)	Conversion [b] (%)	TF [b] (h^{-1})
1 [c]	supported [Sn(TPyP)]$^{2+}$	4.0	15	6.1	115
2 [c]	supported [Sn(TPyP)]$^{2+}$	5.5	20	7.0	120
3 [c]	supported [Sn(TPyP)]$^{2+}$	5.0	25	11.0	207
4 [c]	supported [Sn(TPyP)]$^{2+}$	4.8	30	15.3	295
5 [c]	supported [Sn(TPyP)]$^{2+}$	6.5	40	6.1	87
6 [c]	supported [Sn(TPyP)]$^{2+}$	6.5	50	3.0	43
7 [d]	supported [Mn(TPyP)]$^+$	5.0	20	3.1	67
8 [d]	supported [Mn(TPyP)]$^+$	5.0	30	6	132
9 [d]	supported [Mn(TPyP)]$^+$	5.5	40	7	152
10 [d]	supported [Mn(TPyP)]$^+$	5.0	50	6	132

[a] All reactions were conducted in toluene (9.0 ml) using cyclohexene (1.0 ml, 0.98 M) and NaBH$_4$ (1.0 g, 0.026 mol).
[b] Based on cyclohexene oxidation to 2-cyclohexen-1-one.
[c] Using 0.34 g sample, yielding 0.0106 M concentration of [Sn(TPyP)]$^{2+}$ in reaction solution.
[d] Using 0.10 g sample, yielding 2.0 $\times$ 10^{-4} M concentration of [Mn(TPyP)]$^+$ in reaction solution.

metalloporphyrin catalysts to function [24,39–41]. However, the presence of $NaBH_4$ may be disadvantageous in another way. Decomposition of the metalloporphyrin molecules in both higher and lower oxidation states is reported to occur in homogeneous systems [2]. In this work it has been noticed that the cyclohexene oxidation reaction does not reach completion when conducted using homogeneous or supported $[Mn(TPyP)]^+$ or $[Sn(TPyP)]^{2+}$.

The catalytic activity of the supported metalloporphyrin complexes after recovery has been investigated. Table 3 shows the values of TF measured for fresh and recovered supported metalloporphyrin catalyst samples used for cyclohexene aerobic oxidation. In both supported $[Mn(TPyP)]^+$ and $[Sn(TPyP)]^{2+}$ the recovered supported catalyst showed lower activity than the fresh one. This is consistent with the preceding discussion about the possible catalyst decomposition under the reaction conditions.

The temperature affected the rate of the cyclohexene oxidation reaction. In both of the supported $[Mn(TPyP)]^+$ and $[Sn(TPyP)]^{2+}$ catalytic systems, the rate of the cyclohexene oxidation reaction increased with increasing temperature in the range 10–30°C. At temperatures higher than 30 or 40°C, the reaction slowed down, as appears from values of TF in Table 4. Similar behaviours are known for other metallo-

porphyrin-catalysed olefin oxidations [21,24]. Therefore, unless otherwise stated, all catalytic reactions were conducted at 30°C. The trend of increasing rate with temperature is not unusual in catalysis, and reflects the activation energy requirements for the catalytic reaction to occur. On the other hand, the lowering in the rate with temperatures higher than 30 or 40°C could be due to the loss of dissolved O_2 molecules from the catalytic mixture at higher temperatures. This would exclude the reactant oxygen. The rate lowering may also be due to the tendency of the metalloporphyrin to decompose under the catalytic reaction conditions when using higher temperatures. The metalloporphyrin decomposition is evidenced from the fact that the supported catalyst partly lost its activity on recovery, vide Table 3. Furthermore, solid state spectral analysis indicated decomposition of the supported metalloporphyrins. UV/visible and FT-IR spectra measured for recovered supported metalloporphyrin samples did not appear clearly, whereas spectra of fresh samples were clearer. Details of solid state spectral analysis have been reported elsewhere [22,23].

The effects of other reaction parameters on the reaction rate were studied. The rate of cyclohexene oxidation reaction was affected by the type of the solvent used. The reaction was immeasurably slow when conducted in polar

Table 5
Effect of concentration [a] of the supported $[M(TPyP)]^{n+}$ on the rate of cyclohexene oxidation to 2-cyclohexen-1-one

Entry	Catalyst	Catalyst concentration [a] $(M \times 10^5)$	Time (h)	Conversion [b] (%)
1	supported $[Sn((TPyP)]^{2+}$	0	4.5	0
2	supported $[Sn((TPyP)]^{2+}$	312	0	4.5
3	supported $[Sn((TPyP)]^{2+}$	676	4.0	5.60
4	supported $[Sn((TPyP)]^{2+}$	1560	4.5	10.10
5	supported $[Sn((TPyP)]^{2+}$	2130	9.8	11.60
6	supported $[Mn(TPyP)]^+$	0	5	0
7	supported $[Mn(TPyP)]^+$	10.0	5	6.00
8	supported $[Mn(TPyP)]^+$	18.0	5	10.00
9	supported $[Mn(TPyP)]^+$	45.0	5	21.00
10	supported $[Mn(TPyP)]^+$	59.0	40	85.00

All reactions were conducted at 30°C in toluene (9.0 ml) using cyclohexene (1.0 ml, 0.98 M) and excess $NaBH_4$ (1.0 g, 0.02.64 mol).
[a] Moles of $[M(TPyP)]^{n+}$ per liter of catalytic solution.
[b] Based on cyclohexene oxidation into 2-cyclohexen-1-one.

solvents, such as N,N-dimethylformamide or tetrahydrofuran. With no solvent (pure cyclohexene), no detectable reaction was observed. Therefore, all reaction runs were conducted in toluene unless otherwise stated.

At this stage, no detailed kinetic study was done for the supported catalytic systems described here. Reaction initial rates were not quantitatively measured with accuracy. Based on measured percent conversion or TF values, preliminary study shows that the cyclohexene oxidation reaction is affected by initial concentrations of the supported catalysts, the olefin and the dioxygen. Table 5 summarizes the effect of varying the concentrations of the supported catalysts $[M(TPyP)]^{n+}$ on the value of reaction conversion. The percent conversion per unit time, measured after 5 h, for the cyclohexene oxidation, increased with higher initial catalyst concentration, in both supported $[Mn(TPyP)]^{+}$ and $[Sn(TPyP)]^{2+}$ systems.

Table 6 shows the effect of varying the initial cyclohexene concentration on the rate of the cyclohexene oxidation to 2-cyclohexen-1-one reaction. The effect exhibited different behaviours in the supported $[Mn(TPyP)^{+}$ and $[Sn(TPyP)]^{2+}$ as expressed in terms of TF values measured after 5 h. In case of the former catalyst, the rate decreased with increasing initial concentration of the olefin. The latter cat-

alytic system behaved in a slightly different manner within the same range of cyclohexene concentration. At 2.0 M or lower initial cyclohexene concentrations, the rate increased with higher concentrations. At 2.0 M or higher, the rate decreased with higher concentrations. No reaction was observed when conducted in pure cyclohexene with no other solvents.

Complete exclusion of air oxygen from the reaction mixture inhibited the oxidation reaction completely. On the other hand, bubbling fast streams of air, through the reaction mixture, slowed down the oxidation reaction. The oxidation reactions occurred only with slow streams of air. Therefore, the results described here were measured using catalytic systems exposed to air without bubbling. Using streams of pure oxygen also inhibited the reaction. The catalyst regained its activity by exposure to nitrogen atmosphere followed by pure oxygen atmosphere. Similar behaviours have already been reported for other homogeneous catalytic systems [14,24]. With higher oxygen concentrations, the dissolved $NaBH_4$ is oxidized without further regenerating the catalytically active species with lower oxidation states [5].

No detailed mechanistic pathways are proposed at this time for the supported catalytic systems described here. Two different mechanisms are proposed for homogeneous metallo-

Table 6
Effect of cyclohexene initial concentration on the rate of cyclohexene oxidation to 2-cyclohexen-1-one

Entry	Catalyst	Cyclohexene initial concentration (M)	Time (h)	TF (h^{-1})
1 [a]	supported $[Sn(TPyP)]^{2+}$	0.49	3.0	157
2 [a]	supported $[Sn(TPyP)]^{2+}$	0.98	4.8	295
3 [a]	supported $[Sn(TPyP)]^{2+}$	1.47	3.0	378
4 [a]	supported $[Sn(TPyP)]^{2+}$	1.98	5.0	142
5 [a]	supported $[Sn(TPyP)]^{2+}$	9.8 [a]	9.0	0
6 [b]	supported $[Mn(TPyP)]^{+}$	0.49	5.0	136
7 [b]	supported $[Mn(TPyP)]^{+}$	0.98	5.0	132
8 [b]	supported $[Mn(TPyP)]^{+}$	1.96	20.0	12
9 [b]	supported $[Mn(TPyP)]^{+}$	9.8 [c]	20.0	0

All reaction runs were conducted at 30°C in toluene (amount varied to keep total volume 10.0 ml) using $NaBH_4$ (1.0 g, 0.0264 mol).
[a] Using 0.34 g sample, yielding 0.0106 moles of $[Sn(TPyP)]^{2+}$ per liter reaction solution.
[b] Using 0.10 g sample, yielding 2.0×10^{-4} moles of $[Mn(TPyP)]^{+}$ per liter reaction solution.
[c] In cyclohexene only with no solvent.

porphyrin-catalysed olefin oxidation reactions, and are presented elsewhere [1–5]. Non-radical chain (non-autooxidation) processes assume that the catalytically active lower oxidation state metalloporphyrin species activates both the dioxygen and the olefin molecules. In this case the metalloporphyrin ring is involved throughout the course of the reaction. Such processes are accepted for metalloporphyrin-catalysed oxidations in the case of linear olefins. In these processes, the reaction may yield the ketonic and the alcoholic products. The ketonic products are again converted into alcohols by the effect of the $NaBH_4$. Autooxidation, on the other hand, involves free-radical chain reactions initiated at the beginning of the reaction by virtue of the metalloporphyrin ring. After the initiation, the metalloporphyrin ring is not directly involved. Such processes are proposed to account for the production of 2-cyclohexen-1-one from cyclohexene [5].

Despite the fact that the non-autooxidation mechanism explains several data observed here, the autooxidation mechanism accounts for the exclusive production of 2-cyclohexen-1-one from cyclohexene in the presence of supported catalytic systems as documented for homogeneous counterparts [2,3,5,10,11]. The fact that the supported catalysts are more selective than their homogeneous counterparts can be rationalized on the basis of this assumption.

The supported metalloporphyrins are expected to follow mechanistic pathways parallel to those proposed for homogeneous [M(TPP)]–$NaBH_4$–O_2 systems [2,3,5,10,11]. In the case of homogeneous catalysis, the non-autooxidation mechanism is believed to yield mixtures of products including the alcohols [5]. The activation of the dioxygen and the olefin molecules is believed to occur at one side of the metalloporphyrin ring [3,42]. The resulting MP/O_2/olefin intermediate yields a variety of ketonic and alcoholic products. Supported metalloporphyrins, on the other hand, have more steric hindrance than their homogeneous counterparts. Therefore, the MP/O_2/olefin complex is less

likely to occur, leaving more room for the autooxidation process to occur. Consequently the production of the 2-cyclohexen-1-one is expected to dominate in the case of supported catalysis.

The study of detailed mechanistic pathways for supported metalloporphyrin-catalysed olefin oxidations is beyond the objectives of this work. We are continuing to study further the mechanisms of these reactions. In addition to supported $[Mn(TPyP)]^+$ and $[Sn(TPyP)]^{2+}$, the catalytic activities of other supported species, such as [Pd(TPyP)], [Fe(TPyP)] and others, are being investigated for the oxidation reactions of a variety of olefins.

4. Conclusions

1. The poly(siloxane)-supported $[Sn(TPyP)]^{2+}$ and $[Mn(TPyP)]^+$ metalloporphyrins selectively catalysed cyclohexene to 2-cyclohexen-1-one under mild reaction conditions.

2. Each of the supported catalysts showed higher activity than its homogeneous counterpart.

3. For practical purposes, the supported $[Mn(TPyP)]^+$ is more favorable than the supported $[Sn(TPyP)]^{2+}$, since the former selectively produced 2-cyclohexen-1-one, even when left for prolonged times.

4. The supported $[Sn(TPyP)]^{2+}$ ion did not catalyse 1-octene oxidation, whereas the supported $[Mn(TPyP)]^+$ ion did.

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