Catalysis Today 141 (2009) 66–71

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Redox and selective oxidation properties of Mn complexes grafted on SBA-15

Lakshi Saikia, D. Srinivas *

National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India

ARTICLE INFO

Article history:
Available online 6 May 2008

Keywords:
Grafted manganese complexes
Mn(TPP)Cl
Mn(Salen)Cl
Organo-functionalized SBA-15
Selective oxidation of limonene
Redox behavior of Mn

ABSTRACT

Manganese complexes of 5,10,15,20-tetraphenylporphyrin (Mn(TPP)Cl) were grafted on SBA-15 functionalized with propyl-amine, -thiol and -sulfonic acid groups. The acido-basic properties of the support influenced the oxidation state, redox behavior and selective oxidation properties of the Mn complexes. Acidic supports (SBA-15-*pr*-SH and SBA-15-*pr*-SO_3H) promoted the reduction of Mn ions in Mn-TPP complexes from 3+ to 2+ oxidation state. A similar behavior was found also when Mn(Salen)Cl complexes were immobilized on those supports. However, the extent of such facile reduction was more in the case of Mn-TPP than in Mn-Salen complexes. The former exhibited superior catalytic activity (turnover frequency) than the latter-type Mn complexes in regio-, stereo- and chemoselective oxidation of *R*-(+)-limonene with molecular oxygen (1 atm) at ambient temperatures. The catalytic oxidation activity correlates with the redox behavior of the grafted Mn complexes.

1. Introduction

One of the aims of immobilizing metal complexes inside the pores of zeolites and zeolitic materials or on the surface of inorganic oxides or carbon-based materials is to develop enzyme-mimic, reusable, solid catalysts with enhanced performance at mild conditions [1,2]. While there has been a significant achievement in the preparation and catalytic use of these materials, the role of the support and its acido-basic properties on fine-tuning the redox behavior of immobilized complexes needs more detailed investigations. Ligand structure, weak molecular interactions and the surrounding protein moiety in metalloenzymes play a crucial role in imposing a specific, unusual molecular geometry and electronic structure to the active site, which further affect its catalytic behavior [3]. The complexes of porphyrins, phthalocyanines and Schiff base have been known to mimic the functionality of metalloenzymes [1,2,4]. Immobilization of these complexes on mesoporous molecular sieves enables development of catalysts for transformation of bulkier-size organic molecules into value-added products. Recently, we had reported [5,6] studies on Mn(Salen)Cl complexes (Scheme 1) grafted on acid and base functionalized SBA-15. In continuation, we now report, for the first time, studies on manganese complexes of 5,10,15,20-tetraphenylporphyrin (Mn(TPP)Cl) (Scheme 1) grafted on propyl-amine, propyl-thiol and propyl-sulfonic acid-functionalized SBA-15 molecular sieves. These materials are superior to the corresponding grafted Mn(Salen)Cl complexes in the regio-, stereo- and chemoselective oxidation activity of *R*-(+)-limonene at ambient temperatures with molecular oxygen (1 atm) as oxidant. The influences of the nature of the support and the ligand structure on the redox behavior and catalytic oxidation properties of the Mn complexes are examined. The materials were characterized by diffuse-reflectance UV–vis, Fourier transform-infrared (FT-IR) and electron paramagnetic resonance (EPR) spectroscopic techniques. Correlations between the catalytic activity and redox properties of the grafted Mn complexes are explored.

2. Experimental

2.1. Material preparation

2.1.1. Mn(TPP)Cl

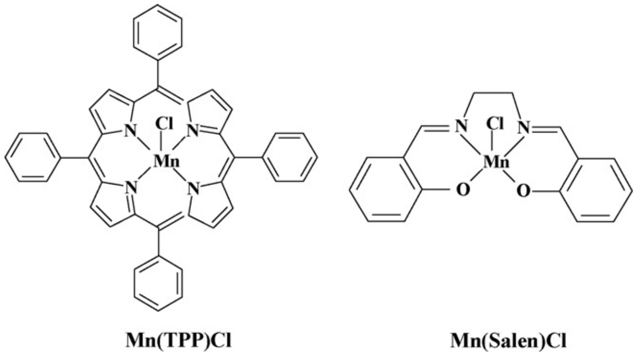
Meso-tetraphenylporphyrin (TPP) was prepared according to the known procedure [7]. An equivalent quantity of distilled pyrrole and reagent grade benzaldehyde were refluxed in propionic acid for 30 min. The mixture was cooled to 298 K and the precipitate was filtered and washed thoroughly with methanol and then with hot water. It was dried in vacuum to get purple colored TPP ligand.

Mn(TPP)Cl was prepared following the method of Adler et al. [8]. In a typical synthesis, 2.5 g of purified TPP was dissolved in 250 ml of *N*,*N*-dimethyl formamide at the reflux condition. To it, $Mn(OAc)_2 \cdot 4H_20$ (2 g) was added. The solution was allowed to reflux for 30–45 min and then, cooled to 298 K. The reaction mixture was poured into an ice-cold NaCl solution (40 g of NaC1 in 500 ml of distilled water). The resulting precipitate was collected

---

* Corresponding author. Tel.: +91 20 2590 2018; fax: +91 20 2590 2633.
E-mail address: d.srinivas@ncl.res.in (D. Srinivas).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.03.014



Scheme 1. Molecular structure of the grafted Mn complexes.

by filtration and washed with 1 l of distilled water. The solid was allowed to dry in air for 15 min. It was, then, dissolved in 250 ml of methanol and the solution was filtered. The methanolic solution was poured into an equal volume of 6 M aqueous HCl solution. The green precipitate formed was filtered and washed with water and dried in air as done previously. It was then, recrystallized from *n*-hexane. The purities of TPP and Mn(TPP)Cl were confirmed by C, H and N analyses and UV–vis and FT-IR spectroscopy techniques.

2.1.2. Grafted Mn(TPP)Cl complexes

Neat SBA-15 and propyl-amine, -thiol and -sulfonic acid-functionalized SBA-15 materials were prepared as reported by us earlier [6]. The organo-functionalized SBA-15 (2 g) was, first, activated at 353 K, under vacuum, for 2 h and then, dispersed in 50 ml of dry-toluene. "Neat" Mn(TPP)Cl (0.30 g) was added and the contents of the flask were refluxed, under nitrogen atmosphere, for 24 h. The solid was filtered, dried at 333 K and Soxhlet-extracted initially, with toluene for 12 h and then, with dichloromethane for another 12 h. The solid Mn catalysts (SBA-15-*pr*-NH_2-Mn(TPP)Cl, SBA-15-*pr*-SH-Mn(TPP)Cl and SBA-15-*pr*-SO_3H-Mn(TPP)Cl, respectively), thus prepared, were dried (353 K and 12 h) and used further in the characterization and catalytic activity studies.

2.1.3. Characterization techniques

The materials were characterized by atomic absorption spectroscopy (AAS), elemental analyses (C, H, N and S; Carlo-Erba 1106 analyzer), X-ray diffraction (Philips-X'Pert Pro; Cu Kα radiation), transmission electron microscopy (TEM; JEOL-model 1200 EX), surface area (BET; NOVA 1200 Quanta Chrome instrument), FT-IR spectroscopy (Shimadzu 8201 PC) and diffuse-reflectance UV–vis spectroscopy (Shimadzu UV-2500 PC) techniques. Electron paramagnetic resonance (EPR) spectra were recorded with a Bruker EMX spectrometer ($\nu = 9.42$ GHz and 100 kHz field-modulation). The spectra were recorded at 80 K using a Bruker BVTB 3500 variable temperature controller.

2.2. Reaction procedure

In a typical reaction, grafted Mn(TPP)Cl, *R*-(+)-limonene, *iso*-butyraldehyde (co-reagent), *N*-methylimidazole (*N*-MeIm; additive) and toluene (solvent) were taken in a double-necked round-bottom flask (50 ml) fitted with a gas-purging unit. The reactions were conducted by bubbling air (1 atm) at a desired temperature and for a desired period of time. The catalyst was separated by filtration and the liquid portion was analyzed by gas chromatography (Varian 3400; CP-SIL8CB column; 30 m-long and 0.53 mm-i.d.). The products were identified by GC–MS (Shimadzu QP-5000; 30 m-long, 0.25 mm-i.d., and 0.25 μm-thick capillary column DB-1). Mass balances were confirmed.

3. Results and discussion

3.1. Structural, spectral and redox properties

Propyl-amine and propyl-thiol functionalized SBA-15 molecular sieves (SBA-15-*pr*-NH_2 and SBA-15-*pr*-SH) were prepared by condensing the surface silanol groups of SBA-15 with 3-aminopropyltrimethoxysilane (APTMS) and 3-mercaptopropyltrimethoxysilane (MPTMS), respectively [6,9]. Oxidation of the thiol groups in SBA-15-*pr*-SH yielded the propyl-sulfonic acid-functionalized SBA-15 (SBA-15-*pr*-SO_3H) [6,10]. Mn(TPP)Cl was then grafted on these organo-functionalized SBA-15 surfaces. Chemical composition and structural and textural properties of the materials are listed in Table 1.

Low-angle X-ray diffraction profiles of the materials revealed that organo-functionalization and grafting of the Mn complexes did not disturb the long-range ordering of SBA-15. Intense (1 0 0) and well-resolved (1 1 0) and (2 0 0) reflections were observed. The *d*-spacing ($d_{1\,0\,0}$) and unit cell parameter estimated from the position of (1 0 0) reflection agree well with the values reported for the related SBA-15 materials [9,10]. Organo-functionalization and grafting of the Mn-complex led to a reduction in the specific surface area (S_{BET}) and pore volume (Table 1). This reduction in S_{BET} on functionalization with a few molecules of modifier (-*pr*-NH_2, -*pr*-SH and -*pr*-SO_3H as well as Mn(TPP)Cl) is, rather, surprising. The value of the *C* constant of the BET equation decreased from 1.05×10^2 (for SBA-15) to 0.78×10^2 and 0.83×10^2 for SBA-15-*pr*-SH and SBA-15-*pr*-SO_3H, respectively. This is because of the elimination of acidic surface OH upon silylation. In such a case, the BET theory does not apply. However, the surface area determined by BJH theory using the cumulative area of the pores also showed a similar decrease as a consequence of organo-functionalization (S_{BJH} (m^2/g): 686, 554 and 546 for SBA-15, SBA-15-*pr*-SH and SBA-15-*pr*-SO_3H, respectively). Apparently, some reconstruction of the solid, which could not be detected, is possibly occurring. Acid and base functionalities affected the surface properties to different extents with the latter affecting to a larger extent than the former. Moreover, concentration of organo-functional group on the surface is another factor affecting the surface modification.

The characteristic UV–vis spectra provided a reliable evidence for the presence of grafted Mn-porphyrin complexes in the catalysts of the present investigation (Fig. 1; left panel). "Neat" Mn(TPP)Cl showed an intense Soret band at 483 nm and Q-bands in the region of 537–618 nm. Upon grafting on the functionalized SBA-15 surfaces, marked changes were observed in the spectra of the Mn complexes (Fig. 1; left panel). The spectral pattern of Mn(TPP)Cl was different on different supports. The Soret band had undergone a blue-shift (from 483 nm for "neat" Mn(TPP)Cl) to 418, 434 and 402 nm for SBA-15-*pr*-NH_2-Mn(TPP)Cl, SBA-15-*pr*-SH-Mn(TPP)Cl and SBA-15-*pr*-SO_3H-Mn(TPP)Cl, respectively). On the contrary, the Q-bands exhibited a red-shift, which is apparently more evident in the spectra of SBA-15-*pr*-SH-Mn(TPP)Cl and SBA-15-*pr*-SO_3H-Mn(TPP)Cl. Such shifts in the Soret and Q-bands positions correspond to a change in the conformation of the porphyrin to an S_4-ruffling geometry [11,12]. 'Neat' Mn(TPP)Cl exhibits a weak d–d band at around 395 nm due to 3+ oxidation state of the Mn. This band is absent in the spectra of SBA-15-*pr*-SH-Mn(TPP)Cl and SBA-15-*pr*-SO_3H-Mn(TPP)Cl. The shifts in the UV–vis band positions and absence of the d–d band indicate that the oxidation state of Mn in SBA-15-*pr*-SH-Mn(TPP)Cl and SBA-15-*pr*-SO_3H-Mn(TPP)Cl decreases from 3+ to 2+. In the FT-IR spectra, the peaks corresponding to the support SBA-15 have masked those of Mn(TPP)Cl (Fig. 1; right panel).

"Neat" Mn(TPP)Cl is EPR-silent at 80–298 K and X-band frequency consistent with the 3+ oxidation of Mn ions. However,

Table 1
Chemical composition and structural properties of Mn(TPP)Cl grafted on functionalized SBA-15

Catalyst	Chemical composition (wt%)[a]					Organic functional group (mmol/g catalyst)[b]	Grafted Mn(TPP)Cl (mmol/g catalyst)[c]	XRD		N_2 adsorption			Wall thickness (nm)
	C	H	N	S	Mn			$d_{1\,0\,0}$ (nm)	Unit cell parameter (nm)	Pore diameter (nm)[d]	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	
SBA-15	0.4	0.9	0	0	0	0	0	9.5	11.0	6.5	692	1.13	5.8
SBA-15-*pr*-SH	6.3	1.8	0	4.7	0	1.5	0	9.9	11.5	6.5	534	0.87	6.3
SBA-15-*pr*-SO_3H	4.8	1.8	0	1.8	0	0.56	0	9.7	11.3	6.2	533	0.83	4.5
SBA-15-*pr*-NH_2	10.9	2.8	3.6	0	0	2.5	0	9.9	11.4	5.9	258	0.4	5.5
SBA-15-*pr*-SH-Mn(TPP)Cl	3.3	3.4	0.7	–	0.06	–	0.011	10.6	12.3	5.7	549	0.66	6.5
SBA-15-*pr*-SO_3H-Mn(TPP)Cl	2.2	2.7	0.6	–	0.09	–	0.016	10.3	12.3	5.8	517	0.72	6.1
SBA-15-*pr*-NH_2-Mn(TPP)Cl	6.2	2.8	2.3	0	0.05	–	0.009	10.6	11.9	6.6	323	0.51	6.5
"Neat" Mn(TPP)Cl	75.4	4.1	8.1	0	2.6	0	–	–	–	–	–	–	–

[a] C, H and N-contents were estimated by elemental analysis. Mn-content was determined by AAS technique.
[b] Determined based on S/N contents.
[c] Determined based on Mn-content.
[d] Determined using the BJH model.

the SBA-15-grafted Mn(TPP)Cl complexes are EPR-active and showed a sextet-line hyperfine pattern centered at $g_{av} = 2.0027$ (Fig. 2). The spectra correspond to an Mn^{2+} species. For a known amount of the material, the intensity of the EPR signal indicative of the concentration of Mn^{2+} ions decreased in the following order: SBA-15-*pr*-SO_3H-Mn(TPP)Cl > SBA-15-*pr*-SH-Mn(TPP)Cl > SBA-15-*pr*-NH_2-Mn(TPP)Cl. Upon grafting, a part of the Mn^{3+} ions in Mn(TPP)Cl got reduced to an EPR-active Mn^{2+} species. Such a reduction in the oxidation state is more favored on acid-functionalized supports like SBA-15-*pr*-SO_3H and SBA-15-*pr*-SH than on base-functionalized supports like SBA-15-*pr*-NH_2 (EPR signal is more intense for the former than the latter complexes; Fig. 2). In other words, the acido-basic properties of the support play a crucial role in fine-tuning the oxidation state and molecular electronic structure of the grafted Mn complexes. Earlier, we had found a similar observation in the case of grafted Mn(Salen)Cl [6]. In those materials, the extent of Mn^{3+} reduction decreased in the order: SBA-15-*pr*-SH-Mn(Salen)Cl > SBA-15-*pr*-SO_3H-Mn(Salen)Cl > SBA-15-*pr*-NH_2-Mn(TPP)Cl. The extent of Mn ions reduction is more in the case of TPP than in Salen complexes. This indicates that not only the support but the nature of the ligand too influences the redox properties of the Mn complexes. Porphyrins (metalloenzyme and photosystem-II, for example) are known to oxidize or reduce readily by chemical, electrochemical or photochemical means forming the corresponding cationic and anionic radical species during the reactions [3]. Such a facile redox behavior of porphyrins and ability to act as an electron-sink makes them versatile to develop efficient redox catalysts. It is known from the electrochemical studies that porphyrin complexes exhibit a more facile redox behavior than the Schiff base–Salen complexes [11,12]. This point once again clarifies the differences in the reducibility of Mn-TPP and Salen complexes on SBA-15 supports.

While the *g*-values were about the same ($g_{av} = 2.0027$), hyperfine coupling constant (*A*), representative of the electron density at the site of Mn, varied in the order of the intensity of the EPR signals. The hyperfine coupling constant (*A*) for SBA-15-*pr*-SO_3H-Mn(Salen)Cl is 97 G and that of SBA-15-*pr*-SH-Mn(Salen)Cl is 95 G. This value for SBA-15-*pr*-NH_2-Mn(Salen)Cl is only 88 G. Since the *A* value is larger for the Mn complexes supported on acidic supports than on basic supports, it indicates that the oxidation behavior of these Mn complexes on acidic supports is also more facile than those on the basic supports.

Earlier, we found that in the case of Mn(Salen)Cl complexes grafted on acidic SBA-15 supports, the Mn^{4+}/Mn^{3+} redox couple

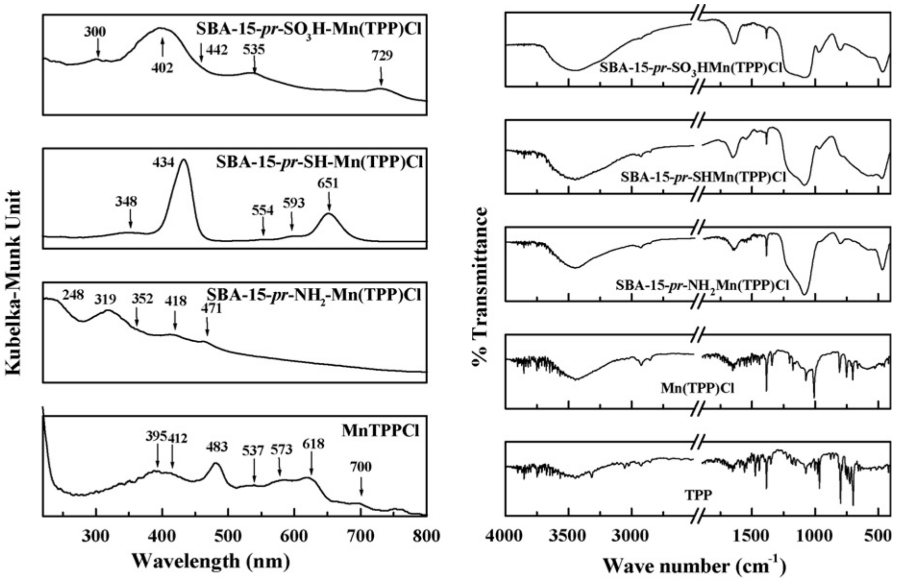


Fig. 1. Diffuse-reflectance UV–vis (left) and FT-IR (right) spectra of 'neat' and SBA-15-grafted Mn(TPP)Cl complexes.

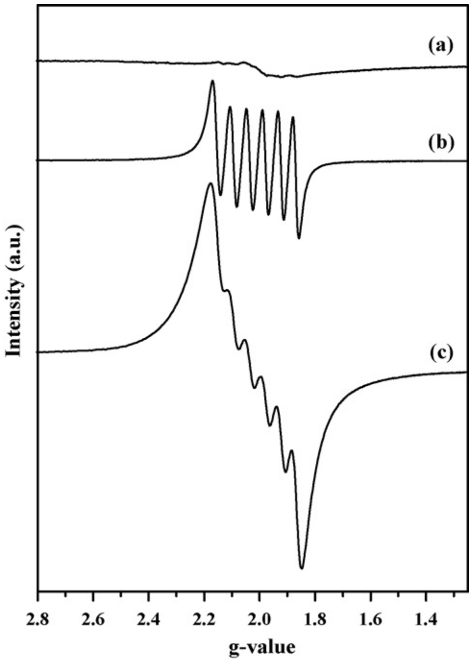
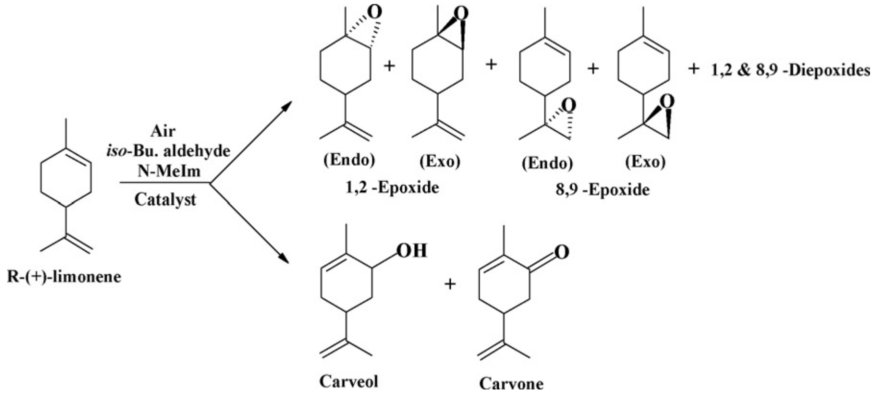


Fig. 2. EPR spectra of Mn(TPP)Cl grafted on (a) propylamine, (b) propylthiol and (c) propylsulfonic acid-functionalized SBA-15.

occurred at less positive $E_{1/2}$ values (+0.697 to +0.728 V) than those grafted on basic propyl-amine support (+0.752 V) [6]. Lower $E_{1/2}$ value is indicative of more facile oxidation and reduction. Hence, an Mn-complex grafted on propyl-thiol/sulfonic acid-functionalized SBA-15 is more easily oxidized/reduced than that grafted on propyl-amine-functionalized SBA-15. Possibly the acidic protons of thiol/sulfonic acid groups facilitate the oxidation/reduction processes. These results agree well with the observations from EPR spectroscopy. Mn(TPP)Cl is dark green in color. Propyl-amine, thiol and sulfonic acid-functionalized Mn(TPP)Cl are of light pink, green and brown colored. The differences in the colors of the complexes are due to variations in their structure and electronic properties. Our earlier studies and those reported in this study on Mn(TPP)Cl complex reveal that the acido-basic properties of the support and ligand structure influence the electronic structure and redox behavior of the immobilized Mn complexes.

3.2. Catalytic activity—selective oxidation properties

Limonene epoxide is a key raw material in the synthesis of pharmaceuticals, fragrances, perfumes and food additives [13]. Conventionally, it is manufactured by oxidation of limonene with stoichiometric amounts of peracids. This method of preparation is not ecofriendly. Limonene is one of the molecules of choice to study chemo-, regio- and stereoselective catalytic oxidations. Oxidation of limonene, in principle, yields a variety of products (Scheme 2). Epoxides will be the selective products if oxidation occurs at olefinic positions. Carveol and carvone will be the products if the oxidation takes place at allylic position. In addition, limonene has two olefinic bonds (1,2 and 8,9) and the oxidation can take place at either or both of these sites (Scheme 2). Further, two types of diastereomers (*endo* and *exo*) are expected for each of the epoxide products. Most of the known solid catalysts [14–18] yield significantly low limonene conversions and epoxide selectivities (20–30%); carveol, carvone and polymeric products are formed in large quantities. The grafted Mn(TPP)Cl complexes are highly efficient for the oxidation of limonene at mild conditions



Scheme 2. Limonene and its oxidation products.

Table 2
Oxidation of *R*-(+)-limonene over SBA-15 grafted Mn complexes[a]

Catalyst	*R*-(+)-limonene conversion (mol%)	TOF (h^{-1})	Product selectivity (mol%)				
			1,2-Epoxide	8,9-Epoxide	1,2- and 8,9-Diepoxide	Carveol	Carvone
“Neat” Mn(TPP)Cl	12.1	34.0	100	–	–	–	–
SBA-15-*pr*-NH_2-Mn(TPP)Cl	30.6	319	88.4	8.1	0.9	1.2	1.4
SBA-15-*pr*-SO_3H-Mn(TPP)Cl	62.1	364	95.0	5.0	–	–	–
SBA-15-*pr*-SH-Mn(TPP)Cl	47.4	346	93.2	5.1	0.9	–	0.8
“Neat” Mn(Salen)Cl[b]	69.1	7.0	97.7	1.2	0.0	1.1	0.0
SBA-15-*pr*-NH_2-Mn(Salen)Cl[b]	75.9	35.4	80.2	6.4	7.2	4.0	2.2
SBA-15-*pr*-SO_3H-Mn(Salen)Cl[b]	60.0	17.8	82.0	8.0	2.6	3.7	3.7
SBA-15-*pr*-SH-Mn(Salen)Cl[b]	64.1	58.9	100	0.0	0.0	0.0	0.0

[a] Reaction conditions: *R*-(+)-limonene = 3.75 mmol; catalyst: MnTPP = 0.036 g (neat) or 0.05 g (grafted), Mn(Salen)Cl = 0.0165 g (neat) or 0.1 g (grafted); iso-butyraldehyde = 9 mmol; *N*-MeIm = 1.7 mmol; oxidant–air = 1 atm (2 ml/min); toluene = 20 ml; reaction temperature = 298 K; reaction time = 8 h.

[b] Data taken from Ref. [6].

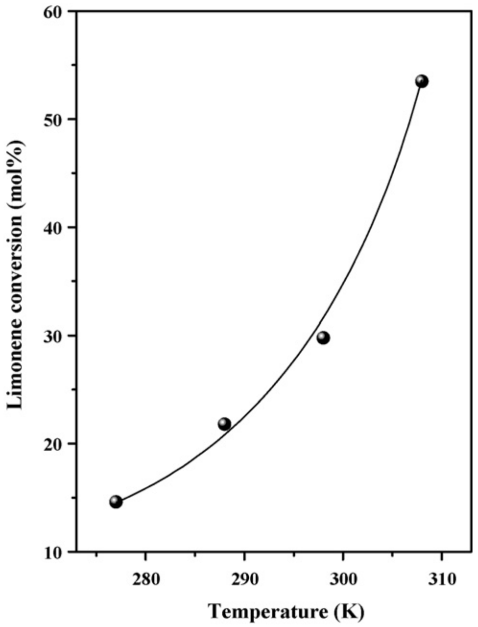


Fig. 3. Influence of temperature on the catalytic activity of SBA-15-*pr*-SH-Mn(TPP)Cl. Reaction conditions: catalyst = 25 mg; *R*-(+)-limonene = 3.75 mmol; *iso*-butyraldehyde = 9 mmol; *N*-MeIm = 1.7 mmol; oxidant–air = 1 atm (2 ml/min); toluene = 20 ml; reaction time = 8 h.

with molecular oxygen as oxidant (Table 2). Epoxide is the main product; the allylic oxidation products formed only in minor amounts. Among the epoxides, the 1,2-epoxide formed with higher (regio-) selectivity. This could be possibly due to differences in the electron density of the olefinic (C_1–C_2) versus the (C_8–C_9) double bonds. The former is more electron-rich due to the neighboring methyl group than the latter. The grafted complexes showed enhanced catalytic activities than the "neat" complex (Table 2). The conversion of limonene increased with the temperature (Fig. 3). However, there was marginal drop in the 1,2-epoxide selectivity from ca., 94 to 84 mol%; 8,9-epoxide and small percentage of carveol and carvone formed at higher temperatures. The grafted TPP complexes were found to be catalytically more efficient than the corresponding Salen complexes. Turnover frequencies are higher by an order of magnitude for Mn(TPP)Cl than for Mn(Salen)Cl complexes (Table 2). The complexes grafted on the acidic supports showed higher catalytic activity and regioselectivity than those grafted on the basic support. Interestingly, this variation in epoxide selectivity follows the variation in electron density and oxidizability of the Mn ions (EPR studies). Apparently, the supports that keep Mn ions in an easily oxidizable environment lead to more efficient selective oxidation catalysts. The percentage diastereomeric excess (de) for these catalysts varied between 22 and 39. A correlation was found between the intensity of the EPR signal, i.e., concentration of the Mn^{2+} species and the catalytic activity (Fig. 4). The higher the concentration of Mn^{2+} complex species the higher was the catalytic activity (turnover frequency) for limonene oxidation. This correspondence, apparently, reveals that supports that keep Mn ions in an easily oxidizable environment lead to more efficient selective oxidation catalysts. Upon reaction with molecular oxygen, the Mn^{2+} ions form high-valent oxo-Mn species. These oxo-species transfer oxygen atom to limonene and undergo self-reduction back to EPR-active Mn^{2+} species [6]. This redox cycle continues and the epoxide is produced selectively. Thus by a proper fine-tuning of the support surface with acidic and basic moieties as well by choosing a right kind of the ligand system (porphyrin, for example) it is possible, in principle, to design highly efficient and selective, solid, mesoporous oxidation catalyst for transformation of organic molecules into value-added chemicals.

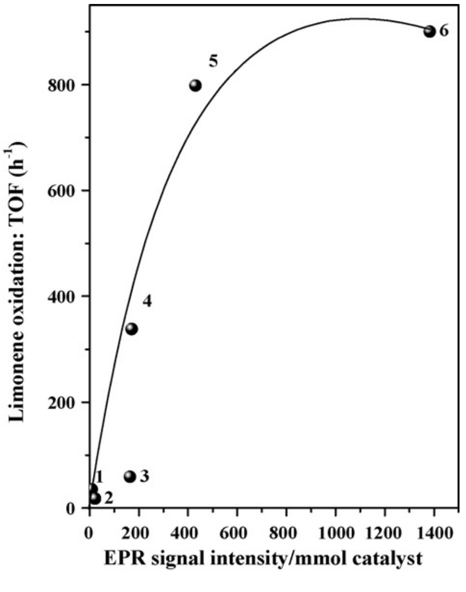


Fig. 4. Correlation between the limonene oxidation activity and Mn^{2+} species concentration (EPR signal intensity) in SBA-15-grafted Mn complexes: (1) SBA-15-*pr*-NH_2-Mn(Salen)Cl, (2) SBA-15-*pr*-SO_3H-Mn(Salen)Cl, (3) SBA-15-*pr*-SH-Mn(Salen)Cl, (4) SBA-15-*pr*-NH_2-Mn(TPP)Cl, (5) SBA-15-*pr*-SH-Mn(TPP)Cl, (6) SBA-15-*pr*-SO_3H-Mn(TPP)Cl. Reaction conditions: catalyst = 25 mg (grafted Mn(TPP)Cl) or 100 mg (grafted Mn(Salen)Cl); *R*-(+)-limonene = 3.75 mmol; *iso*-butyraldehyde = 9 mmol; *N*-MeIm = 1.7 mmol; oxidant–air = 1 atm (2 ml/min); toluene = 20 ml; reaction time = 8 h.

4. Conclusions

Mn(TPP)Cl complexes were grafted on propyl-amine, propyl-thiol and propyl-sulfonic acid-functionalized SBA-15 molecular sieves. These materials were found superior to grafted Mn(Salen)Cl complexes and other known solid catalysts for the selective oxidation of *R*-(+)-limonene to endo-1,2-epoxide with aerial oxygen as oxidant. The reaction occurs at ambient temperatures. Upon grafting, a part of the Mn ions is reduced from 3+ to 2+ oxidation. The extent of such a reduction in the oxidation state of Mn is more in the case of TPP than in Salen complexes and also when the complexes are grafted on acid-functionalized SBA-15 molecular sieves (SBA-15-*pr*-SH and SBA-15-*pr*-SO_3H). There exists a direct correlation between the concentration of the Mn^{2+} species and the catalytic activity. The nature of the support as well the ligand play a crucial role controlling the redox behavior, molecular electronic structure and thereby, the catalytic activity of the Mn complexes.

References

[1] K.J. Balkus Jr., A.G. Gabrielov, J. Incl. Phenom. Mol. Recog. Chem. 21 (1995) 159.
[2] D.E. De Vos, M. Dams, B.F. Sels, P.A. Jacobs, Chem. Rev. 102 (2002) 3615.
[3] H.A.O. Hill, P.J. Sadler, A.J. Thomson (Eds.), Metal sites in proteins and models: iron centers, Structure & Bonding, vol. 88, Springer-Verlag, Berlin, 1997.
[4] D. Brunel, N. Bellocq, P. Sutra, A. Cauvel, M. Lasperas, P. Moreau, F. Di Renzo, A. Galarneau, F. Fajula, Coord. Chem. Rev. 178–180 (1998) 1085.
[5] L. Saikia, D. Srinivas, P. Ratnasamy, Appl. Catal. A: Gen. 309 (2006) 144.
[6] L. Saikia, D. Srinivas, P. Ratnasamy, Micropor. Mesopor. Mater. 104 (2007) 225.
[7] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, J. Org. Chem. 32 (1967) 476.
[8] A.D. Alder, F.R. Longo, F. Kampas, J. Kim, J. Inorg. Nucl. Chem. 32 (1970) 2443.
[9] X. Feng, G.E. Fryxell, L.-Q. Wang, A.Y. Kim, J. Liu, K.M. Kemner, Science 276 (1997) 923.

[10] W.M. Van Rhijn, D.E. De Vos, B.F. Sels, W.D. Bossaert, P.A. Jacobs, Chem. Commun. (1998) 317.
[11] K.S. Suslick, R.A. Watson, S.R. Wilson, Inorg. Chem. 30 (1991) 2311.
[12] A.D.Q. Ferreira, F.S. Vinhado, Y. Iamamoto, J. Mol. Catal. A: Chem. 243 (2006) 111.
[13] B.D. Mookherjee, R.A. Wilson, Encyclopedia of Chemical Technology Kirk-Orthmer, vol. 17, 4th ed., Wiley, New York, 1996, p. 603.
[14] R. Hutter, T. Mallat, A. Baiker, J. Catal. 153 (1995) 177.
[15] H.E.B. Lempers, R.A. Sheldon, Appl. Catal. A: Gen. 143 (1996) 137.
[16] L.E. Firdoussi, A. Baqqa, S. Allaoud, B.A. Allal, A. Karim, Y. Castanet, A. Mortreux, J. Mol. Catal. A: Chem. 135 (1998), 11, 435.
[17] C. Schuster, W.F. Hölderich, Catal. Today 60 (2000) 193.
[18] S. Bhattacharjee, T.J. Dines, J.A. Anderson, J. Catal. 225 (2004) 398.