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Epoxidation of Styrene by Fe, Mn, and V Metalloporphyrins Encapsulated Si, Al, Ti And V- Mcm-41

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Abstract Iron(III), Mn(III) and VO(IV) metalloporphyrin complexes have been encapsulated into ordered hexagonal mesoporous molecular sieves. The encapsulation is effective due to the electrostatic attraction of quaternary ammonium sites present in the porphyrin and the Brönsted/Lewis acid sites present in the mesoporous molecular sieves. These heterogeneous catalysts were catalytically active for the epoxidation of styrene with PhIO exhibiting different selectivity and negligible leaching of active species. The heterogeneous catalysts were reused three times with a slighter decrease in activity but the selectivity patterns were maintained during the recycling experiments.

Keywords Metalloporphyrins · MCM-41 · Heterogeneous catalysts · Styrene epoxidation

1 Introduction

Metalloporphyrins are well known to mimic the activity of enzymatic monooxygenases. Porphyrins and related species have been used as active and versatile catalysts for various reactions involving oxidations [1, 2], hydroxylation [3] and cyclopropanations [4]. Groves et al. [5] have first described the iron(III) porphyrin with iodosylbenzene system as a functional model for cytochrome P-450 for hydrocarbon oxidation. Supporting a metalloporphyrin on an insoluble support has been the goal of several researchers in the past few years [6–9]. Anchoring of these metalloporphyrin complexes onto solid supports leads to easy catalyst recovery, reuse and thus reduces the overall cost of the starting materials.

MCM-41 is an attractive support for metalloporphyrins because it provides a large and tunable pore size, large internal surface area and a regular array of porous channels. The large pore size of these mesoporous materials facilitates the flow of reactant and product molecules in and out of the pore system [10, 11].

The main aim of our studies is to use porphyrin ligands that can be readily attached to solid supports. This has led us to synthesize cationic metalloporphyrins. Among the various methods employed to incorporate metalloporphyrins inside the pores or cavities of the supports, the one based on electrostatic interactions between an ionic metalloporphyrin and counter-charge present on the surface of the carrier is of interesting to the catalytic point of view [12, 13]. Besides the simplicity of the catalyst preparation and the large ionic exchange capability of support generated by the isomorphous substitutions, the existence of strong interactions prevent leaching of the active centers from the support. The porphyrin ligand containing quaternary ammonium ion is selected, which can readily be attached to metal substituted MCM-41, due to the presence of Bronsted/Lewis acid sites. The MCM-41 supports were selected because they are oxidatively stable under the reaction conditions and the investigations of catalytic activity of cationic metalloporphyrins encapsulated into MCM-41 through cation exchange/adsorption/electrostatic interaction. These cationic metalloporphyrins can be anchored to the supports selected through electrostatic attraction.

In this paper we report the catalytic results obtained with [meso-tetrakis(4-trimethylammoniophenyl) porphine]

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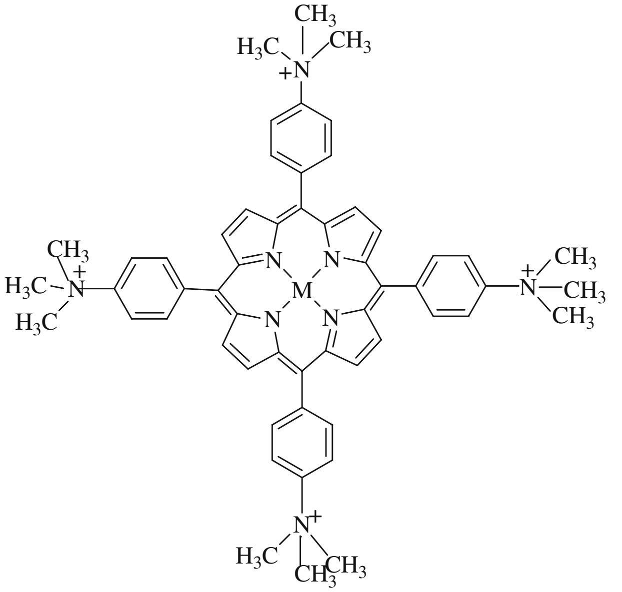


Fig. 1 Structure of cationic metalloporphyrins. (Where, M = Mn(III)Cl, Fe(III)Cl (or) V(IV)O)

(Fig. 1) with different metal centers anchored into Si/Al/Ti/V-MCM-41, in the oxidation of styrene with iodosylbenzene. Apart from the possible interactions between the support and metalloporphyrins mentioned above, strong interactions also possible in the case of water soluble metalloporphyrins containing the quaternary ammonium site and the Brönsted/Lewis acid sites present in Al/Ti/V-MCM-41. The encapsulation method used here offers two advantages [14]: (i) the porphyrin species act as charge compensating ions and are therefore strongly bound to the mesoporous solid support and (ii) the amount of encapsulated porphyrin can be easily controlled simply by an appropriate choice of the Si/M (M = Al/Ti/V) ratio of the mesoporous host.

2 Experimental

2.1 Materials

The following chemicals were used in the synthesis of mesoporous molecular sieves. Sodium metasilicate (Qualigens), tetraethyl orthotitanate (Merck), aluminium sulphate hexadecahydrate (Merck), and vanadyl sulphate (Merck) were used as sources of silicon, titanium, aluminium and vanadium respectively; cetyltrimethylammonium bromide (CTAB) (Spectrochem) is used as the structure-directing agent.

Pyrrole, Propionic acid, 4-dimethylaminobenzaldehyde, nitrobenzene and methyl iodide were purchased from SRL chemicals. Iodosylbenzene was prepared from iodobenzene diacetate (Fluka) following the method described previously [15]. Styrene was purchased from Fluka chemicals.

2.2 Characterization of Samples

FTIR spectra were recorded on a Shimadzu FTIR-8000 spectrophotometer. X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer using Cu-Kα radiation ($\lambda = 1.5406$ Å). Specific surface areas were obtained by the BET method at liquid nitrogen temperature with an Omnisorb 100CX Coulter instrument. FAB+ mass spectrum was obtained on a JEOL SX102/DA-6000 Mass Spectrometer using m-nitro benzyl alcohol (NBA) as the matrix. UV-Vis diffuse reflectance spectroscopy was performed on a Varian CARY 500 spectrometer. The oxidation products were analysed with a Gas Chromatograph (CHEMITO-C) equipped with a HP-5 capillary column. The reaction products were confirmed by GC-MS (Perkin Elmer Instrument, Auto system XL with Turbomass mass spectrometer) and authentic samples.

2.3 Synthesis of Mesoporous Molecular Sieves

Al/Ti/V-MCM-41 mesoporous molecular sieves with variable Si/M ratios were synthesized by using the modified procedure of Beck et al. [16], under the hydrothermal conditions using the following molar ratio: SiO_2:n Al_2O_3 (or) TiO_2 (or) V_2O_5:0.2CTAB:0.89H_2SO_4:120H_2O. Here n = 0 for Si-MCM-41 and 0.007–0.04 for Al/Ti/V-MCM-41.

The resulting product was filtered, washed and then air-dried overnight, finally calcined in air at 550 °C for 6 h.

The samples are designated as: Al-MCM-41(25), (or) Ti-MCM-41(25) (or) V-MCM-41(25) where 25 is the Si/M ratio in the gel and M = Al/Ti/V.

2.4 Synthesis of Cationic Metalloporphyrins

The synthesis of free base porphyrin [meso-tetrakis (4-trimethylammoniophenyl) porphine] tetraiodide, H_2TAPP, was carried out according to previously reported procedure [17]. Water soluble cationic manganese-porphyrin, [meso-tetrakis(4-trimethylammoniophenyl)porphyrinato] manganese(III) pentachloride (MnTAPP) was obtained by the metallation of the free base porphyrin with manganese (II) acetate tetrahydrate in water following the method of Thompson and Krishnamurthy [18] whereas iron insertion (FeTAPP) into the free base porphyrin was achieved by heating H_2TAPP (0.35 mmol) with $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (2.8 mmol) at reflux in water for 5 h.

The cationic oxovanadium(IV) porphyrin, [meso-tetrakis (4-trimethylammoniophenyl)porphyrinato] oxovanadium(IV) tetrachloride (VOTAPP) was obtained by metallation of the free ligand (0.14 mmol) with vanadyl sulphate (1.84 mmol) following the method described by Erdman et al. [19]. After cooling, the solvent was removed under reduced pressure and the dark solid was precipitated by using saturated KI solution. The crystalline metalloporphyrin products, was filtered and dried in a vacuum desiccator to constant weight.

The iodide anion was exchanged quantitatively for chloride using a Dowex 1 × 2-2001—chloride ion exchange resin.

UV-Vis (H_2O), MnTAPP: λ_{max} (nm): 378, 399, 466 (45 860), 562, 594. FAB$^+$ Mass spectrum, $MnC_{56}H_{60}N_8$ m/z 898, cal.av.899.

FeTAPP: λ_{max} (nm) (ε, mol^{-1} cm^{-1}): 413 (55 520), 514, 578, 638. FAB$^+$ Mass spectrum, $FeC_{56}H_{60}N_8$ *m/z* 903, cal.av. 901.

VOTAPP: λ_{max} (nm) (ε, mol^{-1} 1 cm^{-1}): 433 (24 366), 565, 603. FAB$^+$ Mass spectrum, $C_{56}H_{60}N_8VO$ m/z 911, cal.av.912.

2.5 Synthesis of Supported Catalysts

Metallorphyrin supported catalysts were obtained by stirring an aqueous solution containing excess metallorphyrin with Al/Ti/V-MCM-41 (25) at room temperature for 24 h. The glass flask was covered with Al foil to exclude light. The resulting materials were filtered, washed with distilled water in a Soxhlet extractor overnight to remove weakly bound metallorphyrins. The encapsulated metalloporphyrin materials were dried in air at 80 °C. The amount of adsorbed porphyrin was determined as the difference between the amount taken for the exchange experiment and that remaining in the solution after filtering and washing, by using UV-Vis spectroscopy. These heterogeneous catalysts are designated as Al/Ti/V(25)-MnTAPP (or) Al/Ti/V(25)-FeTAPP (or) Al/Ti/V(25)-VOTAPP. For comparison purposes metallorphyrins were also encapsulated into pure Si-MCM-41.

2.6 Catalytic Reaction and Product Analysis

A mixture of styrene (5.0 mmol), iodosylbenzene (0.5 mmol) and catalyst (0.025 mmol) in 6 mL of acetonitrile was stirred in 25 mL glass flask for 24 h at room temperature under nitrogen atmosphere. The solid catalyst was then filtered, and the organic products were analyzed by a Chemito-C gas chromatograph using a HP-5 capillary column, (30 m × 0.32 mm ID; 0.25 μm film thickness) coupled with FID. The carrier gas was nitrogen and the chromatographic conditions were: 80 °C (2 min), 20 °C, 260 °C (5 min), injector temp, 260 °C; detector temp, 280 °C. By injecting the standards in GC, under the identical chromatographic conditions, the products were identified. The reaction products were also confirmed by GC-MS.

3 Results and Discussion

3.1 Physicochemical Characterization of the Catalysts

The encapsulation of manganese, iron and vanadyl porphyrins in the pores of mesoporous molecular sieves was confirmed by XRD, BET surface area, FT IR and UV-Vis spectroscopy. The supported materials turned brown/greenish brown, indicating that the metalloporphyrins catalysts were loaded onto the support. It is assumed that the porphyrin complex is adsorbed into the inner surface of the mesoporous structure, as Soxhlet extraction was used to remove any loosely bound metalloporphyrins.

X-ray powder diffraction patterns of the supported and unsupported catalysts were recordered. Figure 2 shows the XRD pattern of VOTAPP and VOTAPP-MCM-41. Due to encapsulation, no appreciable loss in crystallites was observed. However, the intensities of the (110), (200) and (210) peaks were very much decreased in the 2θ range 3.0–6.0. This shows that even though the long range order of

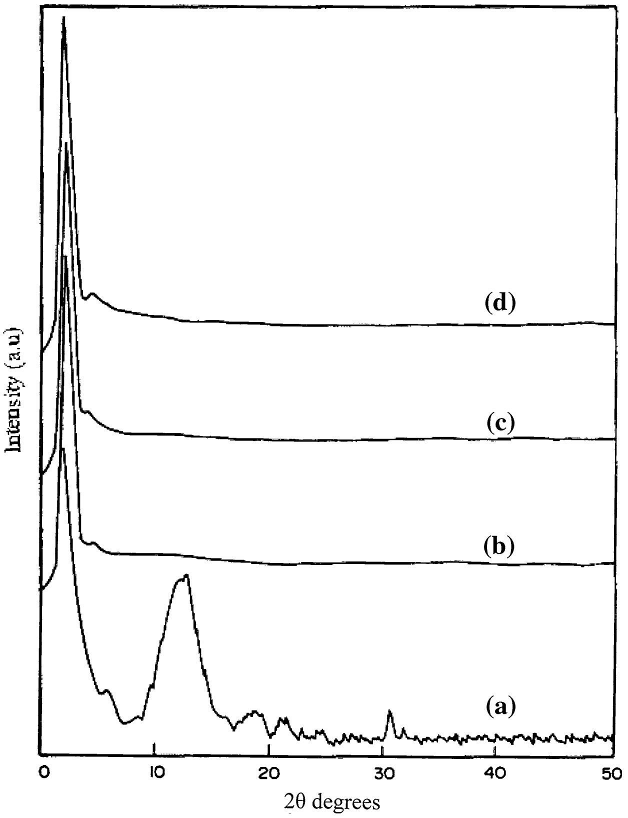


Fig. 2 XRD patterns of (**a**) VOTAPP, (**b**) Al(25)-VOTAPP, (**c**) Ti(25)-VOTAPP, and (**d**) V(25)-VOTAPP

the inorganic supports decreased upon encapsulation, the mesostructure of the supports were still maintained. The absence of XRD peaks associated with Mn(III), Fe(III) and VO(IV) porphyrins crystallites demonstrated that the metalloporphyrins were highly dispersed in the mesoporous matrix. This suggests that the solid supports were structurally unchanged and the Mn(III), Fe(III) and VO(IV) porphyrins should be dispersed molecularly within the channels of mesoporous MCM-41 materials. The results obtained are in excellent agreement with the metalloporphyrins fixated on mesoporous silicates [10, 20].

The BET surface area and pore size of all materials were somewhat lower than that of the unsupported calcined mesoporous materials. For example, Al(25)-FeTAPP has a lower BET surface area (845 m^2/g), and average pore size (28.1 Å) compared to the unsupported Al-MCM-41(25), (910 m^2/g, 29.2 Å), (Fig not shown). These results clearly indicate that the metalloporphyrin cations were located predominantly within the internal channel system of Al/Ti/V-MCM-41(25) materials. Thus, the inner pore systems of mesoporous materials are the main reservoir of catalytically active metalloporphyrin species. The results obtained are in excellent agreement with the amine-functionalized metalloporphyrins fixated on Nb-doped mesoporous silicates [10].

The FT IR spectra confirmed the formation and integrity of metalloporphyrin complex inside mesoporous MCM-41 supports. The FT IR spectra of FeTAPP, Al(25)-FeTAPP, Ti(25)-FeTAPP, V(25)-FeTAPP and unsupported V-MCM-41 in the region 2,000–400 cm^{-1} are shown in Fig. 3. The FT IR spectra of encapsulated materials show some differences from that of unsupported MCM-41 in the range 1,600–1,200 cm^{-1}. The presence of FeTAPP in the mesoporous supports is obvious, because its band observed in the region 1,600–1,200 cm^{-1} for the supported catalysts are not observed in the spectrum of unsupported materials. However, the bands at ~1,460, ~1,410 and ~1,590 cm^{-1} are due to the stretching vibrations of the C=C and C=N bonds. The absorptions at 1,608 cm^{-1} (C=N) and 1,465 cm^{-1} (C=C) are observed for free FeTAPP. The marginal shift in the position of the bands corresponding to C=N and C=C indicates changes in the geometry of FeTAPP as a consequence of encapsulation. Such a shift in band positions due to encapsulation was also reported for phthalocyanine complexes [21]. The same trend was observed in all the metalloporphyrin supported catalysts. This suggests that FeTAPP, MnTAPP and VOTAPP are structurally unchanged and uniformly distributed in the Al/Ti/V(25)-MCM-41 mesoporous materials, which prove that the metalloporphyrins preserve their identity even after encapsulation.

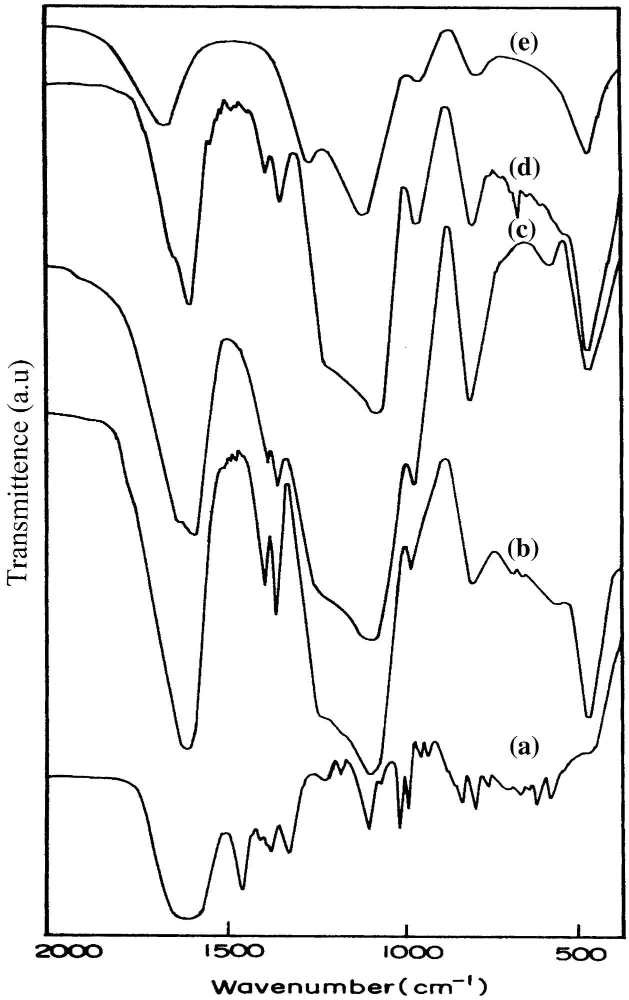


Fig. 3 FT IR spectra of (**a**) FeTAPP, (**b**) Al(25)-FeTAPP, (**c**) Ti(25)-FeTAPP, (**d**) V(25)- FeTAPP, and (**e**) V-MCM–41(25)

In order to observe the presence of metalloporphyrin complexes inside the mesoporous framework, the encapsulated solids were also analyzed by UV-Vis spectroscopy. The UV-Vis spectrum of recovered metalloporphyrins from the filtrate solution after encapsulation on MCM-41 materials have showed no appreciable changes in the wavelength maxima of the Soret absorption and in the relative intensity of the Q bands when compared to the actual spectrum of metalloporphyrins. This may be taken as proof that no chemical changes have occurred to metalloporphyrins during the simple encapsulation procedure used here.

Figure 4 shows the UV-Vis spectrum of VOTAPP in water and supported on MCM-41 materials. The encapsulation of VOTAPP in the MCM-41 framework was confirmed by the presence of characteristic VOTAPP bands in the DRUV-Vis spectra of Al/Ti/V(25)-FeTAPP. The VOTAPP encapsulated samples have the spectrum of the corresponding metalloporphyrin in solution, indicating that the molecular structure of VOTAPP remains intact during the process of encapsulation. However, the diffuse-reflectance UV-Vis spectra of the encapsulated VOTAPP catalysts showed a broad Soret absorption band, which are

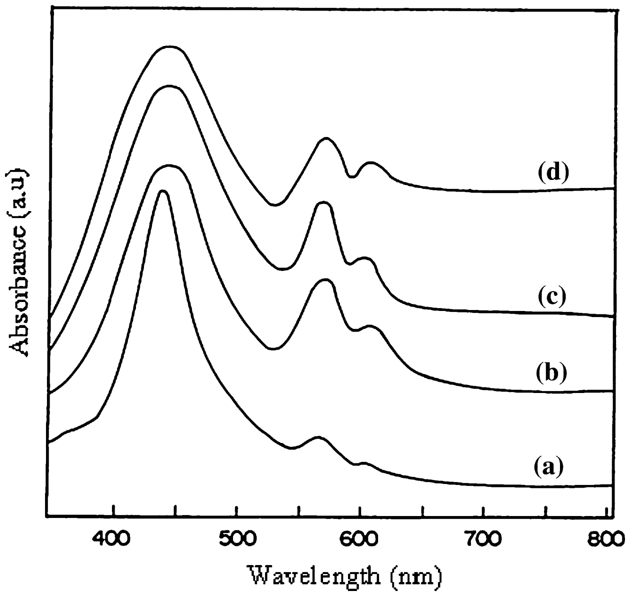


Fig. 4 UV-Vis spectrum of VOTAPP in (**a**) water, (**b**) diffuse reflectance spectrum of Al(25)- VOTAPP, (**c**) diffuse reflectance spectrum of Ti(25)-VOTAPP, and (**d**) diffuse reflectance spectrum of V(25)-VOTAPP

red shifted when compared to the Soret band for the free VOTAPP. This indicates the presence of VO(IV) porphyrins in the mesoporous matrix.

This red shift may be due to the presence of VOTAPP inside the mesoporous materials. Nakagaki et al. showed similar behaviour for zeolite-encapsulated metalloporphyrins compared with their free complexes [22]. The slight red shift and broadening of the Soret band indicates that metalloporphyrin molecules were adsorbed into Al/Ti/V-MCM-41(25) materials. The encapsulated catalysts were prepared by the addition of fixed amount of cationic metalloporphyrins to the meaoporous materials. The amount of encapsulated porphyrin was determined as the difference between the amount taken for the exchange experiment and that remaining in the solution after filtering and washing, by using UV-Vis spectroscopy.

These Al/Ti/V-MCM-41 supports were selected because of their inertness to oxidizing conditions [23]. The cationic porphyrins were found to bind very strongly to these mesoporous materials by cation exchange/adsorption/electrostatic interaction. This was confirmed by stirring the heterogeneous catalysts in CH_3CN, a solvent used in oxidation reactions, for several hours. UV-Vis spectroscopy of such solutions showed no Soret band characteristics of cationic porphyrins. This clearly showed the absence of leaching of porphyrin during the course of the oxidation reactions. This might be due to the strong binding of cationic porphyrins with the mesoporous supports.

Tables 1 and 2 shows the results for the catalytic oxidation of styrene in the presence of the heterogeneous catalysts prepared and with PhIO as oxidant. It is interesting to compare the catalytic activity of the heterogeneous samples prepared with the homogeneous metalloporphyrins and unsupported catalysts. Oxidation of

Table 1 Epoxidation of styrene with PhIO catalyzed by unsupported, homogeneous and cationic metalloporphyrins encapsulated on pure MCM-41[a]

Catalyst	Conversion[b] (%)	Epoxide yield (%)	Selectivity (%)[c]			Turnover number[d]
			SO	BEZ	PA	
Si-MCM-41	0	0	0	0	0	0
Al-MCM41 (25)	0	0	0	0	0	0
Ti-MCM41 (25)	0	0	0	0	0	0
V-MCM41 (25)	7.4	1.2	16.2	83.8	–	2.4
MnTAPP Homogeneous	30.4	24.5	80.6	9.2	10.2	49.0
FeTAPP Homogeneous	34.3	27.3	79.6	12.2	8.2	54.6
VOTAPP Homogeneous	12.5	9.8	78.4	12.0	9.6	19.6
MnTAPP/MCM-41	14.5	13.7	94.5	5.5	–	27.4
FeTAPP/MCM-41	19.5	17.3	88.7	11.3	–	34.6
VOTAPP/MCM-41	11.6	10.5	90.5	9.5	–	21.0

The numbers in the first column indicate Si/M ratios

SO = Styrene oxide; BEZ = Benzaldehyde; PA = Phenylacetaldehyde

[a] Reaction conditions: 0.025 mmol of catalyst, 0.5 mmol of PhIO, 5.0 mmol of styrene in 6 mL of MeCN at room temperature under inert atmosphere; reaction time 24 h

[b] Disappearance of styrene using GC

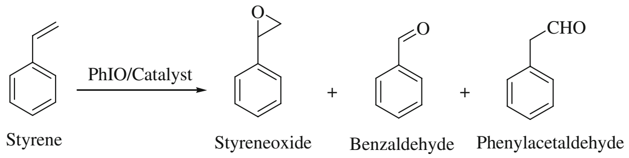
[C] Based on conversion of styrene using GC

[d] Turnover number = mmol epoxide/mmol catalyst

Table 2 Epoxidation of styrene with PhIO catalyzed by Al/Ti/V-MCM-41 encapsulated metalloporphyrin catalysts[a]

Catalyst	Conversion (%)	Epoxide yield (%)	Selectivity (%)			Turnover number
			SO	BEZ	PA	
Al(25)-MnTAPP	44.7	0	–	20.4	79.6	71.2
Ti(25)-MnTAPP	39.8	34.8	87.4	12.6	–	69.9
V(25)-MnTAPP	39.4	36.7	93.1	6.9	–	73.4
Al(25)-FeTAPP	38.6	10.2	26.4	73.6	–	20.4
Ti(25)-FeTAPP	42.4	32.5	76.7	23.3	–	65.0
V(25)-FeTAPP	55.4	48.4	87.4	12.6	–	96.8
Al(25)-VOTAPP	20.3	5.7	28.1	71.9	–	11.4
Ti(25)-VOTAPP	24.5	7.8	31.8	68.2	–	15.6
V(25)-VOTAPP	45.3	28.2	62.3	37.7	–	56.4

[a] Reaction conditions: as in Table 1



Scheme 1 Various oxidation products of styrene

styrene gave styreneoxide, benzaldehyde and phenylacetaldehyde as shown in Scheme 1.

The experimental results illustrated in Tables 1 and 2 confirm that the porphyrin encapsulated heterogeneous systems shows different behavior when compared to their corresponding homogeneous counterparts. The homogeneous system as well as cationic porphyrins supported on Si-MCM-41 produces epoxides as major products. However, metal substituted MCM-41 shows different behaviours. Cationic porphyrins supported on Al-MCM-41(25) produces allylic oxidation products as major products. At the same time Ti(25)-VOTAPP also produces benzaldehyde as major product with styrene. This clearly shows that Brönsted/Lewis acidity introduced by the isomorphous substitution of Si by Al, Ti or V in the mesoporous support or a combined effect of the support and complex plays a major role in the selectivity of the product. Thus encapsulation has a marked effect on the selectivity of the product i.e. the environment of the cationic porphyrin provided by the mesoporous support leads to product selectivity. A similar observation was made in which the environment of the metalloporphyrin provided by the polymer support may lead to substrate or product selectivity [24].

The analysis of data illustrated in Tables 1 and 2 as well as the recycle experiments (Sect. 3.2) revealed that the hexagonal porous structure of MCM-41 mainly responsible for the selectivity patterns obtained, indicating a better accessibility of the catalytic sites. The reaction of styrene with PhIO in the presence of metalloporphyrins encapsulated into Al-MCM-41 produces lower epoxides or no epoxide. This is clearly due to the known higher acidic character of Al-MCM-41 when compared to Ti/V-MCM-41. However VOTAPP supported on Ti-MCM-41 (Table 2, entry 8) also gave comparatively lower epoxide. This shows that the combined effect of guest and host also plays a significant role in the selectivity of products. These experimental results confirm that the ordered hexagonal porosity of the MCM-41 supports which is sufficiently suitable for encapsulating metalloporphyrins favours the substrate to access the catalytic centres as well as the products to diffuse out.

3.2 Recycling Experiments

The stability of the heterogeneous systems prepared was determined by using UV-Vis and FT IR spectrum. The cationic porphyrins encapsulated catalysts were reused successively three times under the same reaction conditions which gave progressive reduction of styrene conversion. The selectivity patterns of various products remain unchanged during the catalytic recycling experiments. However, there was a slight decrease in the observed catalytic activity. These recycling experiments demonstrated the effective heterogenisation of catalysts through strong catalyst-support interactions.

The leaching of the metal complex from the support to the reaction medium was tested by carrying out the following experiments:

(i) the UV-Vis spectra of the reaction solution, after the first run, do not show any absorption peaks characteristic of cationic porphyrins, indicating that leaching of porphyrin complex does not take place during the course of the oxidation reactions. In order to test the leaching of cationic porphyrins, the catalyst was filtered after 5 h reaction, and the filtrate was allowed to react further. In this case also no further reaction was detected, which suggests that leaching of cationic porphyrins into solution does not take place,

(ii) the oxidation reaction was carried out without the substrate but by keeping the other conditions identical (0.025 mmol of catalyst, 0.5 mmol of iodosylbenzene was stirred in 6 mL of acetonitrile in 25 mL glass flask for 24 h at room temperature under inert atmosphere). The filtrate was tested for leaching using UV-Vis spectroscopy. The spectrum shows no characteristic metallopophyrin or free base porphyrin peaks.

(iii) the filtrate collected from experiment (ii) was added to the filtrate obtained after the first run of the cyclohexane and styrene oxidation. This mixture was stirred for 24 h with and without adding fresh amount of oxidant. In this case, the gas chromatography showed no further increase in the conversion of styrene. These experiments confirmed that the cationic metallopophyrins were stably encapsulated within the Al/Ti/V-MCM-41 mesoporous framework.

However, after the third trial the filtrate produced a weak Soret band characteristic of metalloporphyrins, i.e., an approximately 2–3% loss of metalloporphyrins was observed. Hence the marginal decrease in catalytic activity is attributed to leaching and/or decomposition of metalloporphyrins under the reaction conditions. It may also be due to pore blockage, which hinders the easy access of the substrate to the catalyst centre.

FT IR spectra of heterogeneous catalysts recorded after the third run shows band broadening in the region 1,600–1,200 cm^{-1}, which corresponds to the frequency range where bands due to the complex occur. However, the bands typical for Al/Ti/V-MCM-41 framework do not show significant changes after the catalytic reaction. These observations suggest that no structural changes have occurred to the Al/Ti/V-MCM-41 framework during the successive recyclic experiments.

These results clearly showed that the heterogeneous catalysts were active in the oxidation reactions and can be reused without significant decrease in the catalytic activity and almost similar selectivity. These recycling experiments were also used to understand the effect of the support on the stability of cationic metalloporphyrins during the course of the catalytic reaction. The recycled catalysts maintain activity, corresponding to ~90% of the initial value, with almost same selectivity pattern. Thus the support systems not only maintain the selectivity pattern, but also play a major role in the stabilization of the catalytically active cationic metalloporphyrins species.

Thus the FT IR studies confirmed the stability of the support during the course of the reaction and UV-Vis spectra of the filtrate after recycling catalytic reaction showed some metal complex leaching and/or decomposition, which support the results of catalytic, re-use experiments.

4 Conclusion

The synthesis, characterization and catalytic properties of water-soluble manganese, iron and vanadium porphyrin complexes encapsulated in Al/Ti/V-MCM-41 mesoporous molecular sieves have been investigated. The heterogeneous catalysts were prepared by direct encapsulation method by using mesoporous molecular sieves and metalloporphyrins.

The enhanced catalytic activity of the encapsulated complexes is attributed to the fact that the support environment prevents the formation of μ-oxo dimer. Generally, all the metalloporphyrins used in this work, supported on V-MCM-41 produces relatively higher amount of styrene epoxide. At the same time, the metalloporphyrins supported on Al-MCM-41 produce lower amount of styrene epoxide. This clearly shows the role of support environment on product selectivity.

The product distribution for styrene oxidation is also similar for all the catalysts except Al(25)-MnTAPP, which does not produce styrene oxide. Moreover, this is the only catalytic system that produces phenylacetaldehyde. Under homogeneous conditions all the catalysts produce epoxide as major product and phenylacetaldehyde as one of the by-products along with benzaldehyde. However, no other heterogeneous systems produce phenylacetaldehyde except Al(25)-MnTAPP and interestingly this is the only heterogeneous system which does not produce styrene epoxide.

Among the unsupported systems, only V-MCM-41 shows catalytic activity with styrene in the presence of PhIO that produces benzaldehyde as major component.

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