

Spectroscopic and catalytic activity studies of VO(Saloph) complexes encapsulated in zeolite-Y and Al-MCM-41 molecular sieves

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VO(Saloph) complexes, where Saloph = N,N'-*o*-phenylenebis(salicylide naminato), have been encapsulated in microporous zeolite NaY and mesoporous Al-MCM-41 molecular sieves by the "flexible ligand synthesis" method. Upon encapsulation the coordination of VO(Saloph) changes from a square pyramidal to an octahedral geometry. Encapsulation and the pore size have marked effects on the *trans*-stilbene and styrene epoxidation activities of VO(Saloph), with *tert*-butylhydroperoxide as oxidant. The encapsulated complexes are more active (by three to five times) than the "neat" complexes. The encapsulated complexes could easily be separated from the products and the catalysts can be reused. VO(Saloph) complexes encapsulated in Al-MCM-41 are relatively more active than the zeolite-Y-encapsulated complexes. The relaxed geometry of VO(Saloph) and easy access of the active site to the substrate molecules are perhaps responsible for the higher activity of VO(Saloph) encapsulated in Al-MCM-41.

KEY WORDS: Encapsulated vanadium complexes; vanadium Schiff base complexes; epoxidation of styrene and *trans*-stilbene; spectroscopic characterization; catalytic activity of vanadium complexes.

1. Introduction

In recent times, heterogenization/immobilization of transition metal complexes and their use as solid catalysts have been receiving considerable attention, as these novel inorganic materials possess the advantages of both the homogeneous and heterogeneous catalysts [1–5]. Among the various methods of heterogenization, encapsulation of metal complexes inside the pores/cages of zeolite and zeolitic materials has been found to be convenient and advantageous. Several transition metal complexes with Schiff-base [6–8] porphyrin and phthalocyanine [9–10] ligands have been encapsulated in the supercages of large-pore zeolite-Y. Efforts are being made to encapsulate metal complexes in mesoporous silicalite frameworks, to develop materials capable of catalyzing organic transformations with bulkier substrates [11–13]. It was reported that encapsulation enhances the catalytic activity of the metal complexes [14], and in some cases improves product selectivities [15]. It is interesting to investigate the effect of pore size on the structure and activity of the encapsulated metal complex in epoxidation reactions. In view of this, we report here on studies on VO(Saloph) complexes encapsulated in microporous zeolite NaY and mesoporous Al-MCM-41 molecular sieves. The encapsulated complexes were prepared by the "flexible ligand

synthesis" method [16] and characterized by elemental, X-ray diffraction (XRD), Fourier transform infrared (FT-IR), electron spin resonance (ESR) and X-ray photoemission (XPS) spectroscopic techniques. Vanadium complexes have been used in the oxidation of hydrocarbons using oxidants H₂O₂ and TBHP [17–19]. We report here on the epoxidation of *trans*-stilbene and styrene to corresponding oxygenated products with TBHP. The effect of encapsulation on the stability and reactivity of VO(Saloph) is discussed.

2. Experimental

Schiff-base Saloph and "neat"-VO(Saloph) were prepared according to the modified procedure reported earlier [20]. Zeolite-Y-encapsulated VO(Saloph) was prepared using a similar procedure reported earlier [6]. The vanadium content in VO(Saloph)-Y was estimated to be 1.46 wt% (AAS). The C:H:N ratios (6.6:0.36:0.76) are in agreement with the calculated value. VO-Y was prepared by refluxing 7.5 g of NaY (Aldrich, Si/Al = 2.3) zeolite with a 0.02M solution of VOSO₄·5H₂O at a pH of 2.8 for 8 h. The liquid/solid mass ratio during exchange was 93. The solid VO-Y was filtered, washed with warm deionized water and dried at 363 K in an air-oven. The vanadium content in VO-Y was 2 wt% (AAS). VO(Saloph)-encapsulated in Al-MCM-41 (VO(Saloph)-Al-MCM-41) was prepared by adding 2 g of VO-Al-MCM-41 to a solution of 0.4 g of Saloph

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dissolved in 80 ml *tert*-butanol (AR). The suspension was refluxed for 8 h. The solid was filtered out and Soxhlet extracted with *tert*-butanol and acetonitrile (AR). The vanadium content in VO(Saloph)-Al-MCM-41 was estimated to be 2.14 wt% (ICP-AES). The C:H:N ratios (9.84:0.58:1.16) are in agreement with the calculated value. VO-Al-MCM-41 was prepared by refluxing 2 g of Al-MCM-41 with a 0.03M vanadyl sulfate solution for 3 h. The vanadium content in VOAl-MCM-41 was 2.3 wt% (AAS). Al-MCM-41 was synthesized by the standard procedure. The Si/Al ratio was found to be 38 (XRF, Rigaku 3670E). XRD, nitrogen adsorption and TEM (JEOL Model 1200 EX) have confirmed the hexagonal mesoporous MCM-41 structure.

The C, H and N analysis of “neat”-VO(Saloph) was done on a Carlo Erba (Model EA 1108) elemental analyzer. An atomic absorption spectrometer (AAS; Hitachi Model Z-8000) and an inductively coupled plasma atomic emission spectrometer (ICP-AES) estimated the vanadium content in the samples. The X-ray diffraction measurements of the encapsulated complexes were carried out using a Rigaku Miniflex diffractometer with $\text{Cu K}\alpha$ radiation. The textural properties of zeolite-Y and Al-MCM-41 catalysts were determined from N_2 adsorption isotherms measured on an Omnisorb 100 CX Coulter instrument. The FT-IR spectra of the samples were recorded on a Shimadzu (Model 8201PC) spectrophotometer. XPS measurements were made, at 298 K, on a VG Microtech Multilab-ESCA 3000 spectrometer, equipped with a twin anode of Al and Mg and using $\text{Mg K}\alpha$. ESR spectra were recorded at 77 and 298 K on a Bruker EMX spectrometer operating at X band frequency ($\nu \approx 9.78$ GHz) and 100 kHz field modulation. ESR spectral simulations and manipulations were done using the Bruker Simfonia and WINEPR software packages.

Oxidation was carried out by taking a known amount of substrate (1.8 g *trans*-stilbene or 1.05 g styrene, Aldrich), catalyst (“neat”-VO(Saloph) = 5 mg; VO(Saloph)-Y = 50 mg, VO(Saloph)-Al-MCM-41 = 20 mg), TBHP (Merck, 70% solution in water; 2.56 g) and acetonitrile (15 g) in a 50 ml round-bottom flask, immersed in an oil bath and fitted with a water-cooled condenser. The reactions were conducted at 363 K. The progress of the reactions was monitored by a gas chromatograph (Shimadzu 14B; FID detector; SE-52 capillary column). The identities of the products were confirmed by GC-MS (Shimadzu GCMS QP 5000).

3. Results and discussion

Figure 1 shows the XRD patterns of VO-Y, VO(Saloph)-Y, Al-MCM-41 and VO(Saloph)-Al-MCM-41. No appreciable loss in crystallinity was observed as a consequence of metal-complex encapsulation. However,

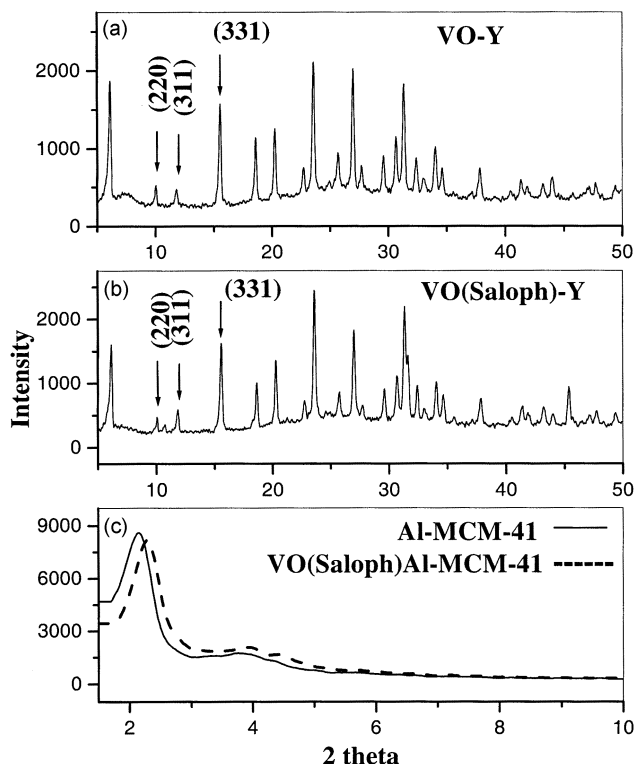


Figure 1. XRD patterns of (a) VO-Y, (b) VO(Saloph)-Y, (c) Al-MCM-41 and (d) VO(Saloph)-Al-MCM-41.

changes were noticed in the intensities of the (331), (311), (220) peaks of zeolite-Y. In NaY (not shown) and VO-Y (figure 1(a)), the relative intensities of the peaks varied in the order (331) > (220) > (311), indicating a random distribution of the exchangeable cations within the zeolite lattice. However, in VO(Saloph)-Y (figure 1(b)), the peak intensities varied in the order (331) > (311) > (220), suggesting displacement of cations in the supercages by the Saloph complexes [17]. The XRD patterns of Al-MCM-41 reveal that the mesoporous structure is retained even after the encapsulation (figure 1(c) and (d)).

The textural properties (surface area, pore volume and average pore diameter) of the encapsulated complexes were determined from the N_2 -sorption studies carried out at 77 K. Upon encapsulating VO(Saloph), the surface area of zeolite-Y and Al-MCM-41 decreased from 836 to 473 m^2/g and from 950 to 540 m^2/g , respectively. Also, a decrease in pore volume of zeolite-Y from 0.42 to 0.24 ml/g was observed. The average pore diameter of Al-MCM-41 decreased from 23 (in Al-MCM-41) to 11 Å. The reduction in the pore diameter is due to pore blockage by VO(Saloph) molecules.

The FT-IR spectra (figure 2) confirmed the formation and integrity of VO(Saloph) complexes inside zeolite-Y and Al-MCM-41. The assignments of a few representative bands are given in table 1. In the spectra of zeolite-encapsulated complexes the bands due to VO(Saloph) were weak and masked by the zeolite bands due to the

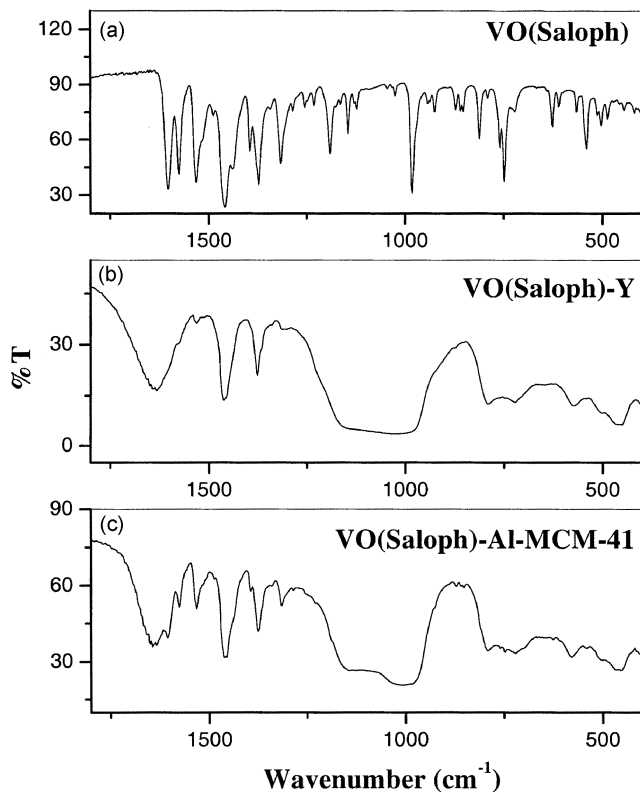


Figure 2. FT-IR spectra (Nujol mull): (a) "neat"-VO(Saloph); (b) VO(Saloph)-Y; and (c) VO(Saloph)-Al-MCM-41.

low concentration of the former. However, in VO(Saloph)-Al-MCM-41 the ligand vibrational bands were comparatively more intense. The marginal shift in the position of the bands corresponding to C=N, C=O and C=C (table 1) indicates changes in the geometry of VO(Saloph) as a consequence of encapsulation. Such a shift in band positions due to encapsulation was also reported earlier in other Schiff-base and phthalocyanine complexes [4,16]. In the case of Cu(Saloph) and Mn(Saloph) complexes the bands due to $\nu(\text{C}-\text{O})$ occurred at 1339 and 1284 cm^{-1} [21]. However, in VO(Saloph) this band appeared at 1370 cm^{-1} (table 1). The shift in the band position toward the lower energy side (VO(Saloph) > Cu(Saloph) > Mn(Saloph)) suggests that the metal-ligand bond is more covalent in VO(Saloph) than in Cu(Saloph) and Mn(Saloph) complexes.

The X-ray photoemission spectra of "neat"-VO(Saloph), VO(Saloph)-Y and VO(Saloph)-Al-MCM-41

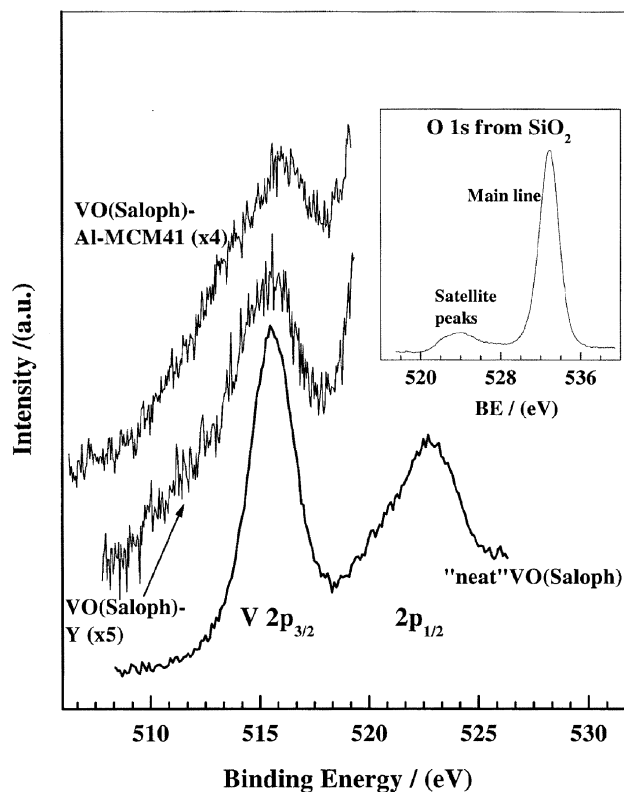


Figure 3. XPS of "neat"-VO(Saloph), VO(Saloph)-Y and VO(Saloph)-Al-MCM-41 from the V2p core level. Inset shows the peaks from the O1s core level of SiO₂.

from the V2p level are shown in figure 4. The inset shows the spectra from the O1s core level of SiO₂. VO(Saloph) exhibits the V2p_{3/2} core level peak at a binding energy of about 516 eV consistent with the +4 oxidation state of vanadium (table 1). The peak from the V2p_{1/2} core level overlaps with the satellite peak from O1s of SiO₂ (figure 3). In encapsulated complexes, the spectra were weak and indicate the location of the complex inside the cages.

Frozen acetonitrile solutions of VO(Saloph) at 77 K exhibited an axial-type ESR spectrum (figure 4(a)). The hyperfine features due to vanadium ($I = 7/2$) are well resolved both in the parallel and perpendicular regions. The spin Hamiltonian parameters ($g_{\parallel} = 1.955$, $g_{\perp} = 1.980$, $A_{\parallel} = 178$ G and $A_{\perp} = 60$ G), obtained by spectral simulations, reveal a square pyramidal geometry for vanadium [22,23]. VO(Saloph)-Y (figure 4(b))

Table 1
Characterization data of "neat" and encapsulated VO(Saloph) complexes.

Catalyst	FT-IR bands (cm^{-1})				BE (in eV)			ESR parameters (at 77 K)			
	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}-\text{O})$	Ring	V2p _{3/2}	N1s ^a	O1s	g_{\parallel}	g_{\perp}	A_{\parallel} (G)	A_{\perp} (G)
VO(Saloph)-neat	1600	1572	1370	1530, 1456	515.7	399.0	530.8	1.955	1.980	178	60
VO(Saloph)-Y	1572	1577	1377	1527, 1461	515.7	398.8	531.8	1.936	1.980	185	75
VO(Saloph)-Al-MCM-41	1604	1578	1377	1531, 1458	516.1	399.0	531.8	1.938	1.980	198	—

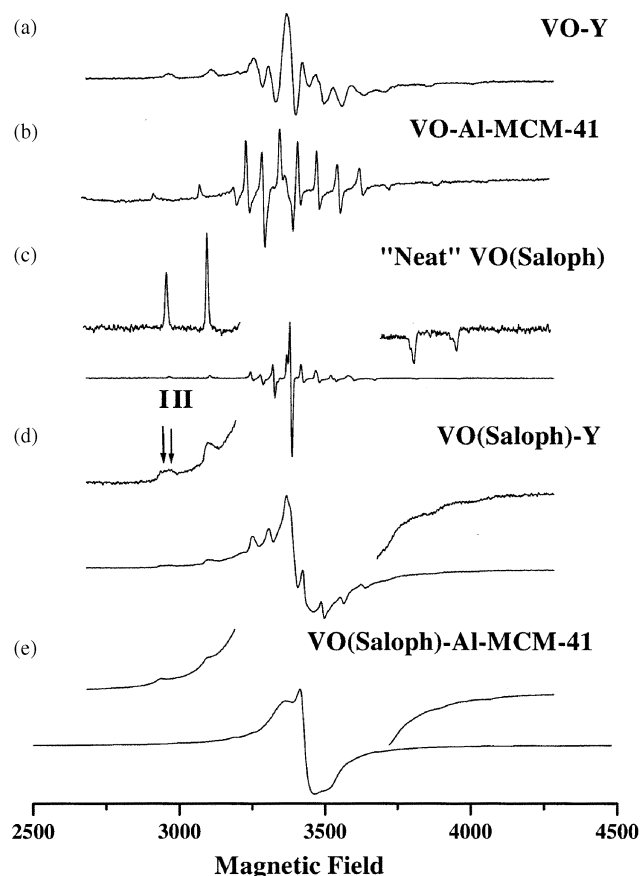


Figure 4. ESR spectra at 100 K: (a) VO-Y; (b) VO-Al-MCM-41; (c) frozen VO(Saloph) in acetonitrile; (d) VO(Saloph)-Y; and (e) VO(Saloph)-Al-MCM-41.

showed spectra attributable to two types of V(IV) species. Species I, characterized by an axial spectrum with spin Hamiltonian parameters $g_{\parallel} = 1.936$, $g_{\perp} = 1.980$, $A_{\parallel} = 185$ G and $A_{\perp} = 72$ G, is attributed to encapsulated VO(Saloph) complexes, and species II, characterized by $g_{\parallel} = 1.944$, $g_{\perp} = 1.980$, $A_{\parallel} = 188$ G and $A_{\perp} = 68$ G, is due to uncomplexed VO^{2+} ions located in the sodalite cages. In VO(Saloph)-Al-MCM-41, the signals were

broad and the vanadium hyperfine features could be barely seen (figure 4(c)); $g_{\parallel} = 1.938$, $g_{\perp} = 1.980$ and $A_{\parallel} = 198$ G). The differences in ESR spectra of “neat” VO(Saloph), VO(Saloph)-Y and VO(Saloph)-Al-MCM-41 are consistent with the increasing vanadium content in the samples (VO(Saloph)-Al-MCM-41 contains 2.14% V while VO(Saloph)-Y has 1.46% V). While the complexes are isolated and confined in the supercages of zeolite-Y, they exhibit weak intermolecular interactions in VO(Saloph)-Al-MCM-41, resulting in broad ESR signals (figure 4(c)). Distinct variations in g and vanadium hyperfine parameters were observed upon encapsulation (table 1). These parameters suggest a distorted octahedral geometry for vanadium in the encapsulated complexes. Perhaps, the zeolites/silica framework provides the sixth-coordination to VO(Saloph). Such interactions were also observed in Cu(phthalocyanine) [24] encapsulated in zeolite-Y.

The catalytic activities of “neat” and encapsulated VO(Saloph) complexes in the epoxidation of *trans*-stilbene and styrene are presented in table 2. The reactions did not proceed in the absence of VO(Saloph). Also, no reaction took place over Al-MCM-41, VO-Y and VO-Al-MCM-41. The encapsulated complexes exhibited higher activity and selectivity compared to “neat”-VO(Saloph). The turnover frequency (number of moles of substrate oxidized per mole of metal per hour; TOF) of VO(Saloph)-Y and VO(Saloph)-Al-MCM-41 was about four and five times greater than that of “neat”-VO(Saloph) (table 2). The reaction was selective (73–88 mol%) for epoxide in *trans*-stilbene oxidation. However, in styrene epoxidation, ring-opened products (e.g., benzaldehyde, etc.) were obtained in significant amounts in addition to epoxide (table 2). Encapsulation has a marked effect on the product selectivity. This is more obvious, in particular, in styrene epoxidation. The yield of styrene epoxide was four to five times greater over the encapsulated complexes than with “neat”-VO(Saloph) (table 2). Among the encapsulated complexes, VO(Saloph)-Al-MCM-41 was more active than VO(Saloph)-Y.

Table 2

Catalytic activities of “neat” and zeolite-Y and Al-MCM-41-encapsulated VO(Saloph) in epoxidation of *trans*-stilbene and styrene with TBHP^a.

Catalyst (weight, mg)	<i>Trans</i> -stilbene epoxidation			Styrene epoxidation				
	Conversion (wt%)	TOF ^b	Epoxide (wt%)	Conversion (wt%)	TOF ^b	Product selectivity (wt%)		
						ald	Epoxide	Others
VO(Saloph) (5)	9.3	256	73.4	10.7	726	32.3	9.4	58.3
VO(Saloph)-Y (50)	36.8	1013	84.8	34.8	2362	11.5	35.5	53.0
VO(Saloph)-Al-MCM-41 (20)	48.1	1324	88.5	40.6	2753	7.7	45.0	47.3
VO(Saloph)-Y (50)-1st recycle	28.2	—	83.0	30.1	—	13.8	27.6	58.6
VO(Saloph)-Al-MCM-41 (20) 1st recycle	32.7	—	87.1	28.9	—	7.5	37.2	55.3

^a Reaction conditions: *trans*-stilbene epoxidation: *trans*-stilbene = 1.8 g (10 mmol), acetonitrile = 15 g, TBHP = 2.56 g (20 mmol), temp. = 363 K, reaction time = 5 h; styrene epoxidation: styrene = 1.04 g (10 mmol), acetonitrile (20 g), TBHP = 2.56 g (20 mmol), temp. = 363 K and reaction time = 2 h.

^b TOF = moles of substrate oxidized per mole of metal per hour.

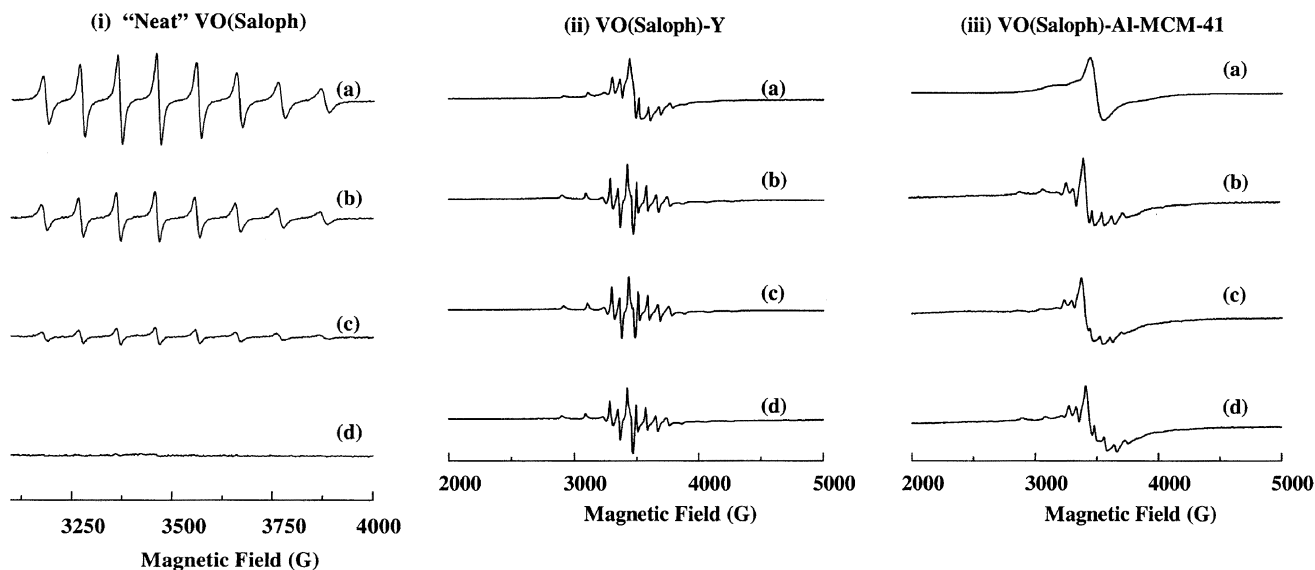


Figure 5. ESR spectra (at 298 K) of reaction mixtures in *trans*-stilbene oxidation: (i) over "neat"-VO(Saloph): reaction time—(a) 0, (b) 30, (c) 60 and (d) 135 min; (ii) VO(Saloph)-Y: reaction time—(a) 0, (b) 2, (c) 4 and (d) 6–24 h; (iii) VO(Saloph)-Al-MCM-41: reaction time—(a) 0, (b) 2, (c) 4 and (d) 6–24 h.

The difference in activity is perhaps due to diffusion limitations in Y-type zeolites or the cage effect. In the reactions with metal Schiff-base complexes in a homogeneous medium one often encounters catalyst deactivation due to formation of oxo-bridged dimer complexes. However, such a deactivation is suppressed on heterogenizing the Schiff-base complexes (table 2). This is evident from the spectroscopic studies (*vide infra*).

The effect of catalyst, substrate and oxidant concentrations and temperature on *trans*-stilbene epoxidation over VO(Saloph)-Al-MCM-41 was investigated. The kinetics data were interpreted using the initial-rate-approach model. The kinetic investigations results revealed a first-order reaction rate dependence with the catalyst and substrate and half-order dependence with the oxidant. From the plot of $\ln(\text{rate})$ versus $1000/T$, the thermodynamic parameters were evaluated to be $E_a = 6.5 \text{ kcal mol}^{-1}$, $\Delta H^\ddagger = 5.7 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 15.8 \text{ cal deg}^{-1} \text{ mol}^{-1}$ and $\Delta G^\ddagger = -0.0042 \text{ kcal mol}^{-1}$.

The mechanism of epoxidation over "neat" and encapsulated VO(Saloph) catalysts with TBHP was investigated by *in situ* ESR spectroscopy. In the reactions with "neat"-VO(Saloph), a known quantity of the reaction mixture was taken out at different time intervals and subjected to the spectroscopic studies. However, with the encapsulated catalysts, the reactions were performed for a specific period of time and then the catalyst was separated, dried and characterized by ESR. Representative spectra of "neat" and encapsulated VO(Saloph) as a function of reaction time are shown in figure 5(i)–(iii). For reactions in a homogeneous medium using "neat"-VO(Saloph), the intensity of vanadium ESR signals decreased with time and disappeared at 135 min (figure 5(i); trace d). In the absence of substrate (stilbene) the signals disappeared at 105 min itself. Interestingly, the encapsulated catalysts

(VO(Saloph)-Y and VO(Saloph)-Al-MCM-41) were ESR active even after 24 h (figure 5(ii) and (iii); trace d).

VO(Saloph) forms vanadium peroxo complexes on interaction with TBHP. The peroxo complex transfers one of its oxygen atoms to the substrate and itself gets converted into an oxo-hydroxo or dioxo-vanadium species. In the homogeneous medium these species can further react, ultimately forming ESR inactive μ -oxo-vanadium(IV) complexes [25,26]. The latter are catalytically inactive. However, in the solid catalysts, VO(Saloph) molecules are well separated due to confinement in the cages or interactions with the support as revealed from ESR studies, and they remain active throughout the reaction (figure 5(ii) and (iii); trace d). Although the formation of such catalytically inactive μ -oxo complexes during the reaction and the advantage of heterogenizing metal complexes in suppressing the formation of such inactive species was postulated earlier, it has not been proved, so far, experimentally. Site isolation of the complex inside Na-Y and Al-MCM-41 stabilizes the monomeric complex and prevents the conversion of catalytically active oxo-hydroxo or dioxo-vanadium species to catalytically inactive μ -oxo bridged dimer, hence giving high TOF. The *in situ* spectral characterization unequivocally establishes this hypothesis.

4. Conclusions

VO(Saloph) complexes encapsulated in zeolite-Y and Al-MCM-41 exhibited high catalytic activity and selectivity in the epoxidation of *trans*-stilbene and styrene. Among the encapsulated complexes, VO(Saloph)-Al-MCM-41 was more active than VO(Saloph)-Y. This difference in activity is attributed to a diffusional limitation cage-size effect. *In situ* ESR studies revealed that

encapsulation enhances the stability of VO(Saloph) complexes during the oxidation reaction by suppressing the formation of catalytically inactive μ -oxo-vanadium species.

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