Oxyfunctionalization of limonene using vanadium complex anchored on functionalized SBA-15

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Abstract

VO(Salten) complexes, where Salten = 3-[*N*,*N'*-bis-3(salicylidenamino)ethyltriamine], have been covalently anchored on to functionalized SBA-15. The formation and integrity of the complex have been confirmed by elemental analysis, FT-IR, X-ray diffraction (XRD) and BET measurements and the complex was used for the oxyfunctionalization of limonene in presence of urea hydroperoxide (UHP) as the oxidizing agent. The oxyfunctionalization of limonene resulted in limonene oxide, carvone, carvacrol and carveol. Anchored complex showed better catalytic activity than the neat complex, while the neat complexes has deactivated in the reaction due to formation of inactive α-oxo-bridged dimers, the covalently anchored complexes remained stable throughout the reaction. The anchored complex could be easily separated from the products and could be reused.
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1. Introduction

Although ample number of reactions of olefin oxidation catalysed by metal complexes has been developed as important synthetic methods, there is very little information in the literature concerning their applications in natural product synthesis. Selective oxyfunctionalization of monoterpenes represents an interesting route to extend the utilization of these cheap natural products. Some of their oxygenated derivatives are commercially important materials for pharmaceutical, flavor and perfumery industry as well as useful synthetic intermediates and chiral building blocks [1,2]. Among these compounds, limonene, α-pinene and β-pinene are the most abundant and are suitable feedstock for the production of carvone, verbenone and myrtenal, respectively, which are important compounds for the flavor and fragrance industry. Due to this importance several groups have been working on the oxidation of these monoterpenes [3–8]. We

have earlier reported the allylic oxidation of α-pinene to its oxygenated products using bis-salicylaldehyde-*o*-phenylene-diimine (Saloph) and substituted (Cl, Br and NO₂) Salophs of ruthenium and cobalt in zeolite-Y [9]. Chromatographic analysis revealed that the main oxidation products of limonene were the 1,2-limonene epoxides and the other products were carvone and geometric isomers of carveol. It was found that in all systems the starting monoterpenes as well as the primarily formed products could undergo various concurrent transformations, such as isomerization, hydrogenation, cyclization, addition, with the balance between the reaction pathways being delicate. Efforts were made to investigate the effects of the reaction variables and the catalyst composition on the product distribution in order to find the most favorable conditions for selective syntheses of desired products [10,11]. Karim and co-workers have studied the synthetic, mechanistic aspects, scope and limitations of selective palladium-catalyzed functionalization of limonene [12]. Various catalytic combinations were examined in order to select the most efficient system for conversion of limonene into allylic esters, ethers or alcohols in acetic acid, methanol and water, respectively.

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It appears that under mild conditions the chemoselectivity was always high as only oxidation products were formed. Moreover, by a judicious choice of ligands and/or reoxidant of palladium, the reaction can be directed mainly towards the formation of functionalized compounds having their allylic double bond in either exocyclic or endocyclic position. In both cases, the *trans*-isomer was the major product. In order to explain these results, a mechanism was proposed involving an external nucleophile attack on a bis-(*p*-allyl-*p*-olefin) palladium complex, which was isolated under acetoxylation reaction conditions.

Limonene was efficiently and selectively oxidized by dioxygen at 60–80 °C in glacial acetic acid containing LiCl, in the presence of the PdCl$_2$–CuCl$_2$ catalytic combination, giving *trans*-carveyl acetate as the major product [13]. Several concurrent transformations of limonene occur in the reaction solutions, i.e., isomerization, acetic acid addition and allylic oxidation. The effect of the reaction variables on the products distribution and reaction rates have been studied and the most favorable conditions for the carveyl acetate synthesis have been found. The use of catalytic system based on MnIII(Salen) complex for the oxidation of limonene with iodosobenzene as terminal oxidant has been reported [14]. For reactions conducted in CH$_2$Cl$_2$ at room temperature, with molar ratio of 1:0.05:1 (limonene:catalyst:iodosobenzene) limonene oxidation does occur with an optimum conversion of 60%. The major products were *cis*- and *trans*-1,2-epoxy limonene (30 and 16.7% selectivity, respectively), the two diastereoisomers of 1-*p*-menthen-9-al (20% selectivity) and carvone (10% selectivity). The higher selectivity towards epoxide formation supports the rebound oxygen mechanism.

In this paper, we have aimed at investigating the possibility of using anhydrous urea peroxide (UHP) as the oxygen source for the oxidation of limonene using VO(Salten) complex covalently anchored on SBA-15 through an organic moiety. The structure of the support was retained after anchoring the complex. Based on the spectroscopic evidences it was envisaged that the complex retains its structure inside the channels and it hangs like a pendant inside SBA-15. These inorganic–organic hybrid materials offer great scope as catalysts for the oxofunctionalization of limonene.

2. Experimental

2.1. Materials

Tetraethylorthosilicate (TEOS), poly(ethylene oxide), poly(propylene oxide), poly(ethylene oxide), Pluronic P123 [EO$_{20}$–PO$_{70}$–EO$_{20}$], 3-chloropropyl triethoxysilane (CPTES), salicylaldehyde, di-ethylene triamine, VOSO$_4$ and limonene were procured from Aldrich. Hydrochloric acid, urea and H$_2$O$_2$ were obtained from Merck. All the solvents were of AR grade and were procured from s.d. fine Chemicals, India and were distilled and dried before use.

2.2. Synthesis

2.2.1. Si-SBA-15

Si-SBA-15 was synthesized following a similar procedure reported in the literature [15]. The SBA-15 used in this paper has been synthesized from a typical synthesis batch with the composition of 4 g Pluronic P123 $M_{avg} = 5800$ [EO$_{20}$–PO$_{70}$–EO$_{20}$], 120 g of 2 M HCl and 9 g TEOS. Typically 4 g of triblock co-polymer was dispersed in 30 g-distilled water and stirred for 3 h. To the resultant solution, 120 g of 2 M HCl was added under stirring and finally 9 g of TEOS was added drop wise and the mixture was maintained at 40 °C for 24 h under stirring and then for 48 h at a temperature of 110 °C under static condition in a teflon bottle. The crystallized product was filtered, washed with warm distilled water and dried at 383 K for 24 h and then calcined at 813 K in nitrogen for 12 h and then maintained at 813 K in air for 5 h to completely remove the template. The structure was confirmed by XRD and surface area.

2.2.2. Synthesis of Cl modified SBA-15 (Si-SBA-15-Cl)

Si-SBA-15-Cl was prepared using similar procedure reported in the literature [16]. In a typical surface modification process, Si-SBA-15 was activated (3 g, 423 K) under vacuum and was refluxed in dry toluene (50 ml distilled over freshly cut sodium and dried over zeolite A) with CPTES (3 g) for 3 h under argon atmosphere. The separated solid was washed with diethyl ether and Soxhlet extracted with 250 ml dichloromethane yielding covalently anchored 3-chloropropyl triethoxysilane moieties Si-SBA-15-Cl Fig. 1(a).

2.2.3. Synthesis of Salten = 3-[N,N′-bis-3-(salicylidenamino)ethyltriamine]

The ligand Salten Fig. 1(b) was prepared following similar procedure reported in the literature [17]. In a typical procedure, to an ethanolic solution of salicylaldehyde, a solution of diethyltriamine in ethanol was added in the ratio of 2:1 and the resulting yellow colored solution was allowed to reflux for 3 h. The excess of solvent was removed under vacuum and a dark yellow colored oily product was obtained.

2.2.4. Synthesis of vanadium Salten (VO(Salten))

VO(Salten) was prepared following a similar procedure reported in the literature [17]. In a typical procedure, to an ethanolic solution of VOSO$_4$ (1.25 g in 50 ml ethanol), the ligand Salten (1.55 g in 5 ml ethanol) was added. The blue colored solution immediately turned green. After refluxing for 2 h, the solid was filtered and recrystallized in ethanol.

2.2.5. Immobilization of VO(Salten) over Si-SBA-15-Cl

VO(Salten) was immobilized following similar procedure in our earlier report [18]. To a suspension of freshly dried Si-SBA-15-Cl (1 g) in dry toluene (40 ml), a solution of Salten ligand (0.1 g) in dry toluene (10 ml) was added and the resulting solution was refluxed for 3 h. The yellow colored solid
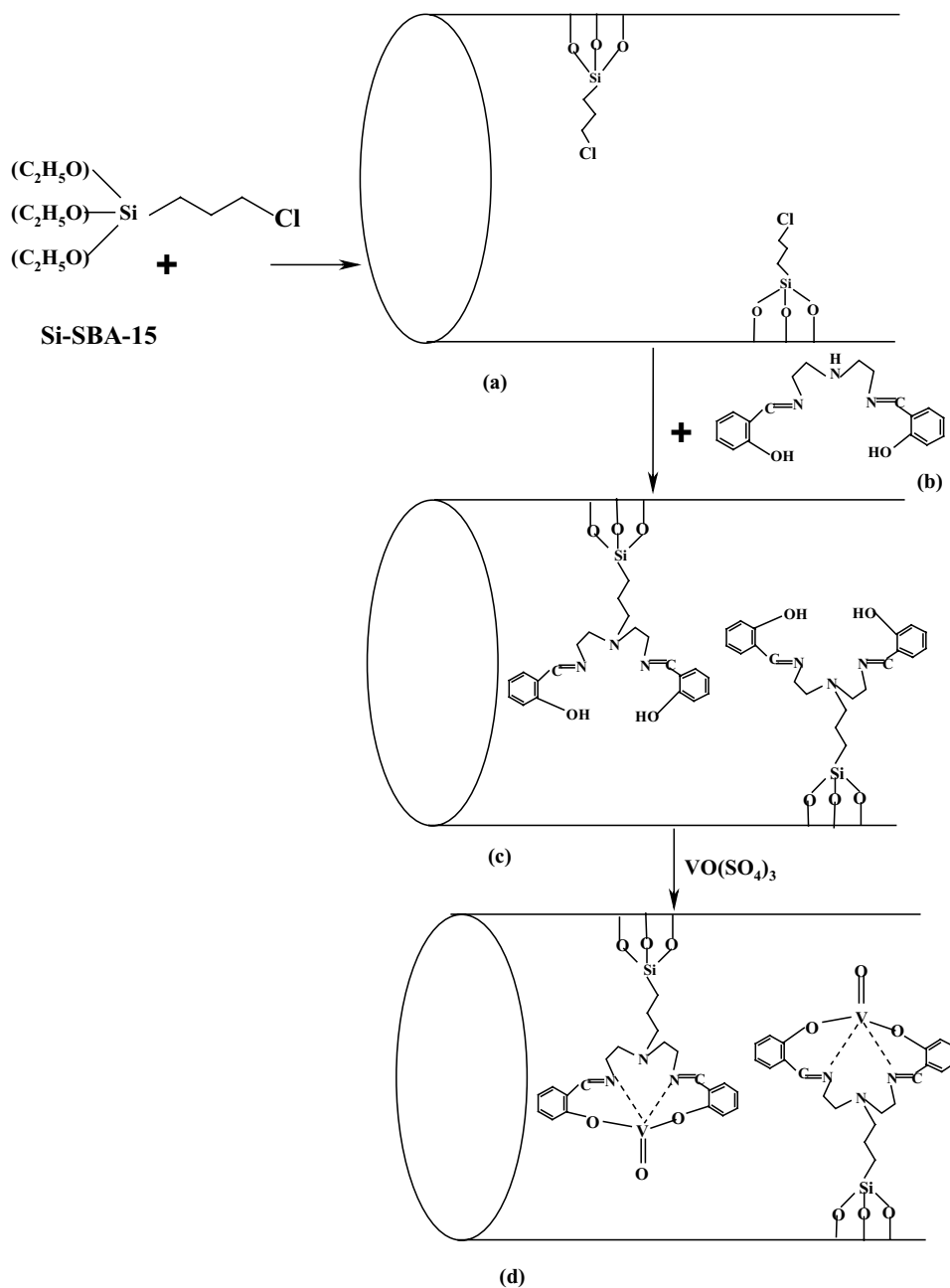
Fig. 1. Synthesis of Si-SBA-15-VO(Salten).

was separated, Soxhlet extracted with anhydrous toluene to remove the unreacted Salten ligand adsorbed on the external surface of Si-SBA-15-Cl and vacuum dried for 24 h. The ligand gets attached to the Si-SBA-15 through the spacer by the nucleophilic displacement of chlorine of Si-SBA-15-Cl by the basic amino group of the ligand (Fig. 1c). Then to a suspension of this solid (1 g) in dry ethanol (40 ml) a solution of $VOSO_4$ (0.1 g) in dry ethanol (25 ml) was added. The solution immediately turned green indicating the formation of a vanadium complex. This was refluxed for 3 h. The green solid (Fig 1d) was separated by filtration, was dried and Soxhlet extracted with dry ethanol and acetonitrile to remove any unreacted vanadium from the surface. The vanadium content

in Si-SBA-15-VO(Salten) was estimated to be 1.2 wt.% by AAS.

2.3. Characterization procedures

The C, H and N analysis of neat-VO(Salten), Si-SBA-15-Cl and Si-SBA-15-VO(Salten) was done on a Carlo Erba (Model EA 1108) elemental analyzer. An atomic absorption spectrometer (AAS; Hitachi Model Z-8000) estimated the vanadium content in the sample. The powder XRD patterns of the SBA-15 materials were collected on a Siemens D5005 diffractometer using Cu Kα ($\lambda = 0.154$ nm) radiation. The textural properties Si-SBA-15, Si-SBA-15-Cl and Si-SBA-

15-VO(Salten) 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.

2.4. Catalytic activity studies

A known amount of substrate (1.36 g limonene), catalyst (neat-VO(Salten) = 3 mg and Si-SBA-15-VO(Salten) = 25 mg), UHP = 1.88 g and acetonitrile = 10 g were taken in a 100 ml round bottom flask immersed in an oil bath and fitted with a water cooled condenser. The reactions were conducted at 50 °C. The progress of the reaction was monitored by withdrawing the samples at different time intervals and analyzed by a Shimadzu 14B series gas chromatograph using a capillary column and FID detector. The samples were also analyzed by GC–MS (Shimadzu GCMS QP 5000) to identify the products.

3. Results and discussion

3.1. Characterization

3.1.1. XRD

The XRD patterns on Si-SBA-15, Si-SBA-15-Cl and Si-SBA-15-VO(Salten) are depicted in the Fig. 2(a–c). The XRD diffraction pattern of Si-SBA-15 shows a very intense peak (1 0 0) and two additional high order peaks with lower intensities (Fig. 2a). This indicates a significant degree of long range ordering of the structure and well formed hexagonal pore arrays. On modification with CPTES, some loss in the intensities of the peaks were observed revealing that silyla-
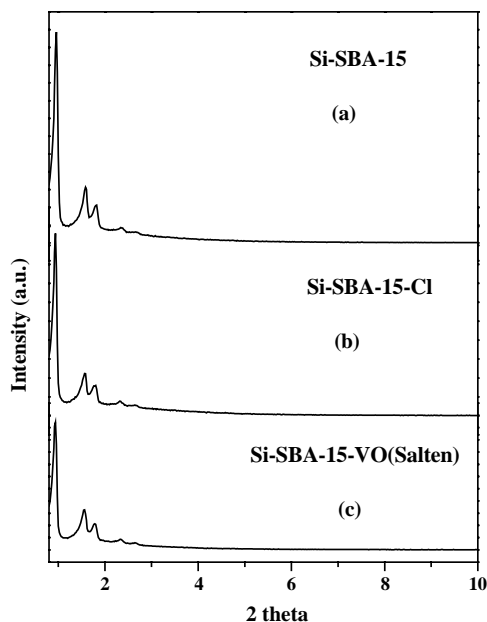

Fig. 2. XRD patterns of: (a) Si-SBA-15, (b) SBA-15-Cl and (c) Si-SBA-15-VO(Salten).

Table 1
Sorption studies

Catalyst	Surface area ($m^2 g^{-1}$)	Pore volume ($ml\,g^{-1}$)/ pore diameter (Å)
Si-SBA-15	980	90
Si-SBA-15-Cl	820	80
Si-SBA-15-VO(IV)Salten	660	76

tion has indeed occurred inside the mesopores of Si-SBA-15 (Fig. 2b). However, it is evident from XRD that in addition to the very intense peak (1 0 0), the two higher order peaks were still observed indicating that the silylation procedure did not diminish the structural ordering of Si-SBA-15. No significant loss in the intensity was observed on immobilizing the vanadium complex.

3.1.2. Sorption studies

Nitrogen adsorption data for the various immobilized complexes on SBA-15 is presented in the Table 1. On modifying Si-SBA-15 with 3-CPTES, the surface area of Si-SBA-15 decreased from 980 to 820 m^2/g and the pore diameter reduced from 90 to 80 Å. Upon immobilizing VO(Salten), a further reduction in the surface area from 820 to 660 m^2/g and pore diameter from 80 to 76 Å were observed. The reduction in the surface area and pore diameter is due to the lining of the walls of Si-SBA-15 with the organic moieties. Similar trend has also been observed previous studies [19].

3.1.3. FT-IR

The FT-IR spectra (Fig. 3) confirmed the formation and integrity of the covalently anchored VO(IV)Salten complex. In the spectra of covalently anchored complex, the bands due to VO(Salten) are weak and masked by the Si–OH bands due to the low concentration of the former. A marginal shift in the positions of the bands corresponding to C=N, C=C and C=O is due to covalently anchoring of the complex.

3.2. Catalytic activity

The results of oxidation of limonene by anhydrous UHP using neat and covalently anchored VO(IV)Salten complex is presented in the Table 2. The products of oxidation of limonene are shown in the Fig. 4. In the absence of the catalysts, no allylic oxidation products are detected. The covalently anchored complex gave better conversion than the neat VO(IV)Salten complex (Table 2). In the reactions with metal Schiff base complexes in homogeneous medium one often encounters catalyst deactivation due to formation of oxo-bridged dimer complexes, which has been proved by spectroscopic studies in our previous paper [20].

The balance between the reaction pathways is delicate. Thus, when the reaction is carried out using 10 ml acetonitrile as solvent, with a molar ratio of limonene to UHP as 1:2 and 25 mg of Si-SBA-15-VO(IV)Salten at a temperature of 323 K, a maximum limonene conversion of 45% and a selectivity of 35% for limonene oxide, 22% for carvone, 19% for
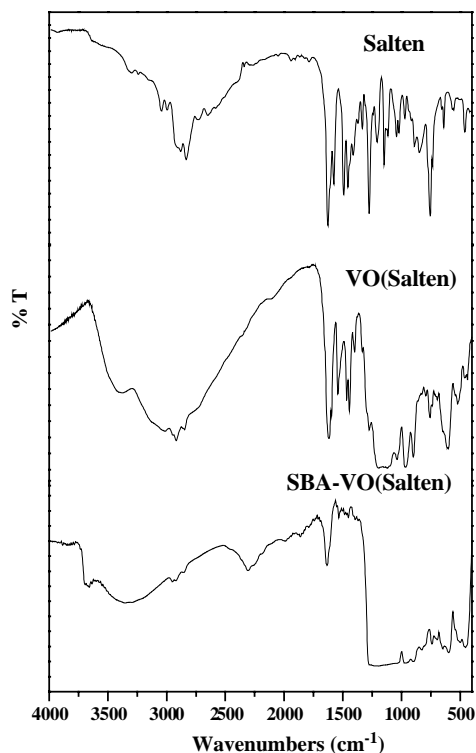
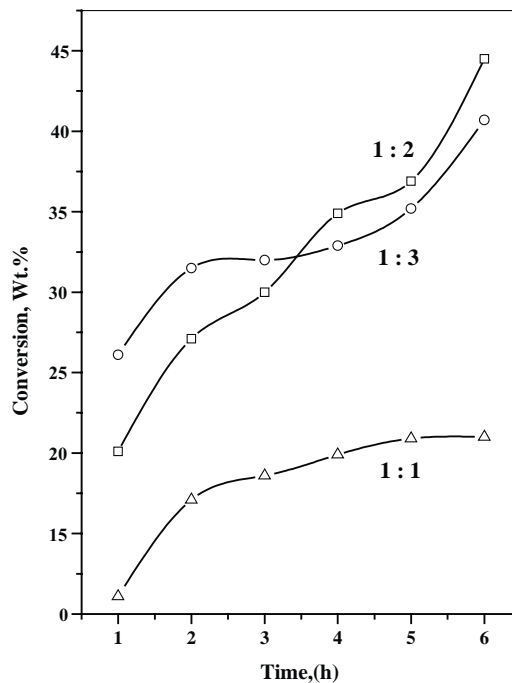Fig. 3. FT-IR spectra in flurolube: (a) Salten, (b) neat VO(Salten) and (c) Si-SBA-15-VO(Salten).

Fig. 5. Effect of limonene to UHP mole ratio on the oxidation of limonene. Reaction conditions: catalyst = VO(IV)Salten-Si-SBA-15 = 25 mg, acetonitrile = 10 g and temperature = 323 K.

carvacrol, 16% for carveol and 7% for unknown product is observed in 6 h. The products distribution depended strongly on the reaction conditions and reaction time.

The reaction conditions have been optimized towards maximum conversion of limonene by varying different parameters. The results are shown in the Figs. 5–9. In Fig. 5, the effect of limonene/UHP mole ratio on the limonene conversion as a function of reaction time is plotted. It is evident that the conversion of limonene first increases with time on

increasing the ratio of limonene/UHP from 1:1 to 1:2. On further increasing the ratio to 1:3, a slight decrease in conversion is observed, which suggests that large amount of UHP is not required for limonene oxidation. No appreciable change in the selectivity for the products was observed. In Fig. 6, the effect temperature on the conversion of limonene is shown. Limonene conversion gradually increases with time on increasing the temperature from 313 to 323 K. But on further increasing the temperature to 338 K, the conversion increases with time up to 1.5 h and then attains a steady state. This is

Table 2
Catalytic activity of neat and covalently anchored Si-SBA-15-VO(IV)Salten in oxidation of limonene

Catalysts	Conversion (%)	Product selectivity (%)				
		Oxide	Carvone	Carvacrol	Carveol	Unknown product
Neat VO(IV)Salten	5.3	32.5	23.2	16.6	16.1	11.6
Si-SBA-15-VO(IV)Salten	20.1	35.7	23	15.3	18.2	8

Reaction condition: limonene = 1.36 g, catalyst (neat-VO(Salten) = 3 mg and Si-SBA-15-VO(Salten) = 25 mg), UHP = 1.88 g, acetonitrile = 10 g, temperature = 323 K and time = 1h.
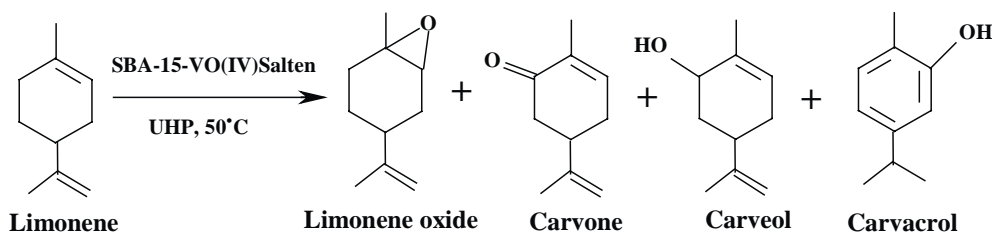

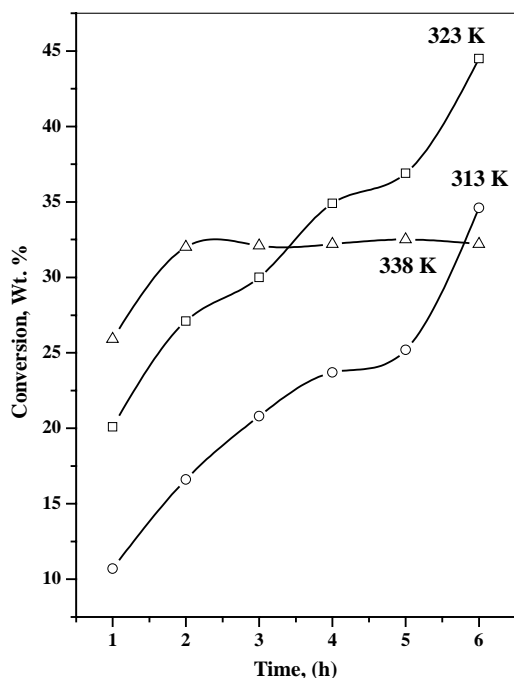Fig. 4. Reaction scheme for oxofunctionalization of limonene.

Fig. 6. Effect of temperature on the oxidation of limonene. Reaction conditions: limonene = 1.36 g, catalyst = VO(IV)Salten-Si-SBA-15 = 25 mg, UHP = 1.88 g and acetonitrile = 10 g.
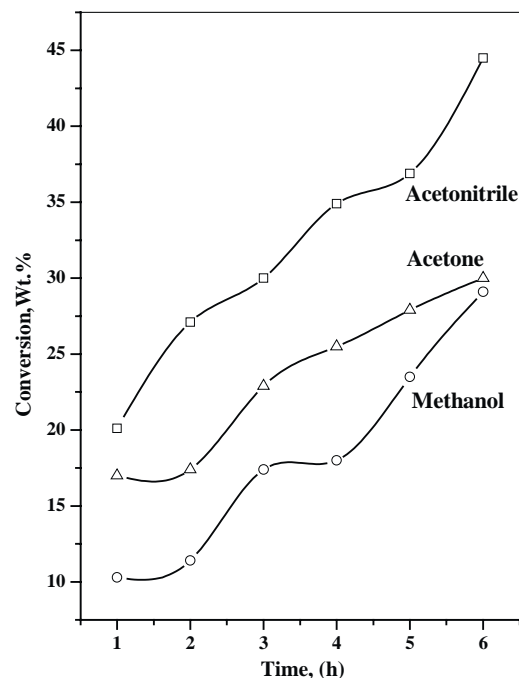

Fig. 8. Effect of solvent on the oxidation of limonene. Reaction conditions: limonene = 1.36 g, catalyst = VO(IV)Salten-Si-SBA-15 = 25 mg, UHP = 1.88 g, temperature = 323 K and solvent = 10 g.

because of the decomposition of UHP at higher temperature. Fig. 7 shows the effect of amount of catalyst on the rate of reaction. It is seen that an increase in the conversion of limonene is observed with time on increasing the catalyst amount from

15 to 25 mg. On further increasing the amount of catalyst to 50 mg, the reaction attains a steady state after 3 h. The effect of different solvents on the oxidation of limonene was studied (Fig. 8). It was observed that acetonitrile was a better
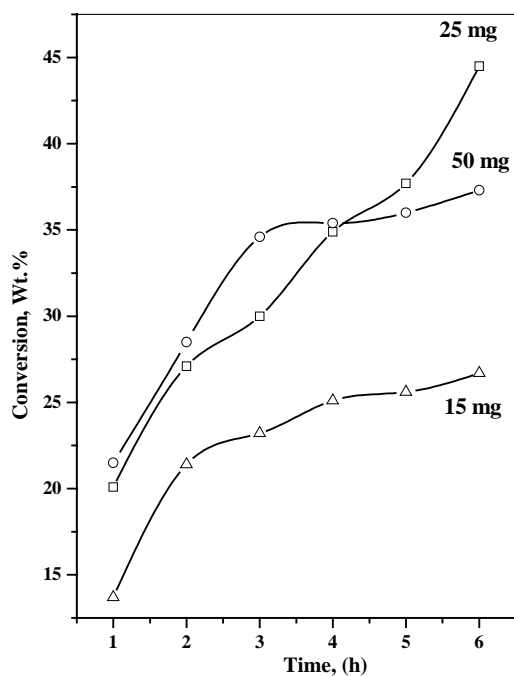

Fig. 7. Effect of amount of catalyst on the oxidation of limonene. Reaction conditions: limonene = 1.36 g, UHP = 1.88 g, temperature = 323 K and acetonitrile = 10 g.
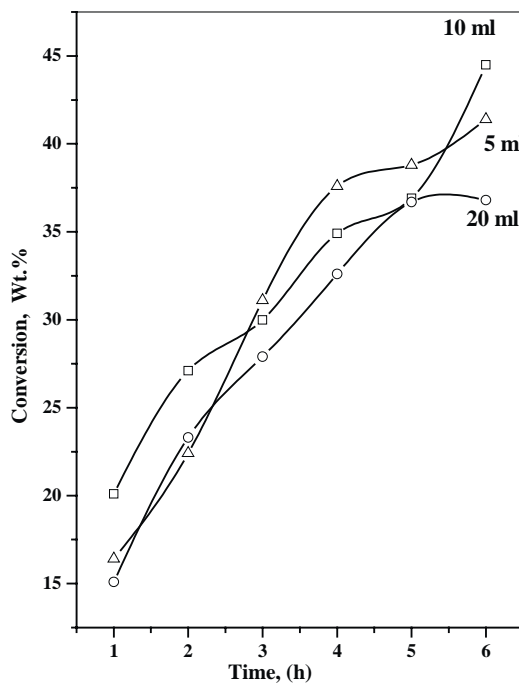

Fig. 9. Effect of amount of solvent on the oxidation of limonene. Reaction conditions: limonene = 1.36 g, catalyst = VO(IV)Salten-Si-SBA-15 = 25 mg, UHP = 1.88 g, temperature = 323 K and solvent = acetonitrile.

solvent compared to acetone and methanol. The selectivity was found to be similar in the case of acetonitrile and acetone but when methanol was used as solvent dramatic changes in the product selectivites was observed. The selectivities for epoxide, carvone and carveol were comparatively less and the selectivity for the unknown product was more.

4. Conclusions

Covalently anchored VO(Salten) complex exhibited high catalytic activity in the oxidation of limonene using anhydrous urea hydro peroxide. The catalytic studies revealed that anchoring of VO(Salten) on functionalized SBA-15 enhances the stability of VO(Salten) complexes during the oxidation reaction by suppressing the formation of inactive μ-oxo-vanadium species. This covalently anchored complex proved to be efficient catalyst for the oxidation of limonene.

Acknowledgement

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