

Epoxidation of alkenes using immobilized vanadyl Schiff base complex on montmorillonite as an efficient recyclable heterogeneous catalyst with *tert*-butyl hydroperoxide

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Abstract

Oxovanadium(IV) Schiff base complex of N,N'-bis(5-[(triphenylphosphoniumchloride)-methylsalicylidinenaphthal-diamine]) was synthesized, characterized and immobilized on sodium montmorillonite as a heterogeneous catalyst. The neat Schiff base complex and supported complex were characterized by X-ray diffraction spectroscopy, IR spectroscopy, diffuse reflectance spectroscopy and atomic absorption spectroscopy techniques. The diffuse reflectance spectra data and IR spectra of the supported Schiff base complex show that the complex was physically entrapped within sodium montmorillonite. The novel heterogeneous catalyst shows excellent catalytic activity in epoxidation of olefins using *tert*-butylhydroperoxide in acetonitrile. In this report, the supported vanadyl complex exhibited 100% selectivity for epoxidation with 91% and 90% conversion for cyclohexene and cyclooctene, respectively. The supported oxovanadium(IV) complex gave higher percent of conversion of olefins than neat oxovanadium(IV) Schiff base complex.

Keywords: Immobilization; Heterogeneous catalyst; Vanadyl Schiff base; Epoxidation; Montmorillonite

1. Introduction

Alkene epoxidation is the interest of many researchers for the synthesis of fine chemicals. Because of their versatility as intermediates, epoxies are of great value in both synthetic organic chemistry and chemical technology.

Transition metals Schiff base complexes are important powerful homogeneous catalysts in the oxidation of organic compounds by various oxygen atom donors. These complexes have been used in epoxidation of olefin, oxidation of alkane, alcohol and thiol as homogeneous catalysts, electrocatalysis, amines oxidation and biological studies [1-3]. The interest in the vanadium complexes has grown over the last few

decades, due to the role of vanadium in catalytic [4-6] and biological [7-9] processes. Recently, several studies on the preparation and catalytic reactivity of vanadyl tetradentate Schiff base complexes have been reported [10-13].

Most of the time, application of the homogeneous catalysts on industrial scale has been prevented due to difficult separation and regeneration of the catalyst from the reaction mixture. Immobilization of the homogeneous catalysts onto solid supports has been the subject of a lot of research in catalytic fields because of long catalytic lifetime, easy separation, thermal stability, high selectivity and easy recyclability [14-16]. A general strategy for converting a homogeneous

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process into a heterogeneous one is to anchor the soluble catalyst on to large surface area inorganic supports [17, 18]. Many different solid catalysts such as zeolites, metal oxides can heterogenized homogeneous catalysts [19, 20]. Mixed metal exchanged zeolite, ion exchange resins and polymerized complexes have been used in liquid phase epoxidation of olefins [21-23]. Recent trends in immobilization of catalyst complexes on clay-based materials such as montmorillonite, zeolites and bentonite appear to be a fantastic method of heterogenization of homogeneous catalysts [24].

Recently, the studies of catalytic activity of immobilized V(IV) Schiff base complexes with *tert*-butyl hydroperoxide (%70 in water) have been reported. Joseph has reported the encapsulation of VO(Saloph) as a heterogeneous catalyst for epoxidation of trans-stilbene and styrene with TBHP (%70 in water) as an oxidant [25]. In the other work, Maurya has reported the synthesize polymeric oxovanadium(IV) complexes as a heterogeneous catalyst and study of catalytic potential for the oxidation of styrene, cyclohexene and trans-stilbene using *tert*-butyl hydroperoxide (%70 in water) as an oxidant [26].

In this work, it has been attempted to use sodium montmorillonite as the host material for immobilization of vanadyl tetradentate Schiff base complex, {[VOL]Cl₂, L: (N, N'-bis(5-[(triphenylphosphonium)-methyl-salicylidine)naphthal-diamine])}. The resulting catalyst has been characterized by using different techniques and has been tested for the selective epoxidation of cyclooctene, cyclohexene, styrene, indene, α -pinene, 1-octene using *tert*-butyl hydroperoxide (70%aqueous) as oxidant.

2.1 2. Experimental

2.2 Materials and physical measurements

All the solvents used were purified using known procedures. Sodium montmorillonite was obtained from Fluka and 3-formyl-4-hydroxy benzyltriphenyl phosphonium chloride have prepared according to literature procedures [27]. 1,8-naphthal-diamine, Cyclooctene and cyclooctene epoxide were purchased from Aldrich Chemical Company. ¹HNMR spectra

were recorded using a Bruker FT NMR 500 (500MHZ) spectrophotometer (CDCl₃ and (CD₃)₂SO. Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elementar-Analyses system, GmbH). Atomic absorption analysis was carried out on a shimadzu 120 spectrophotometer. The purity of the solvents, cyclooctene, cyclohexene, styrene, indene, α -pinene, 1-octene and analysis of the oxidation products was determined by gas chromatography using Agilent7890 with a capillary column and FID detector. Column temperature was programmed between 180°C and 200 °C (2°C/min). Nitrogen was used as carrier gas (40 ml/min) at injection temperature. FT-IR spectra were obtained by Shimadzu 8400S spectrophotometer in KBr pellets. Diffuse reflectance spectra (DRS) were taken on a Scinco 4100 the range 200-1100 nm using BaSO₄ as reference. The powder small angle X-ray diffraction studies were done on ITALSTRUCTURE X-ray diffractometer with CuK α ($\lambda = 1.54\text{\AA}$) radiation. The voltage and current applied to the X-ray tube were 40kV and 30 mA, respectively, with scanning speed as 0.001° min⁻¹. Surface morphology and distribution of particles were studied via VEGA-TESCAN scanning electron microscopy, using an accelerating voltage of 20 kV.

2.3 Synthesis of Schiff base ligand

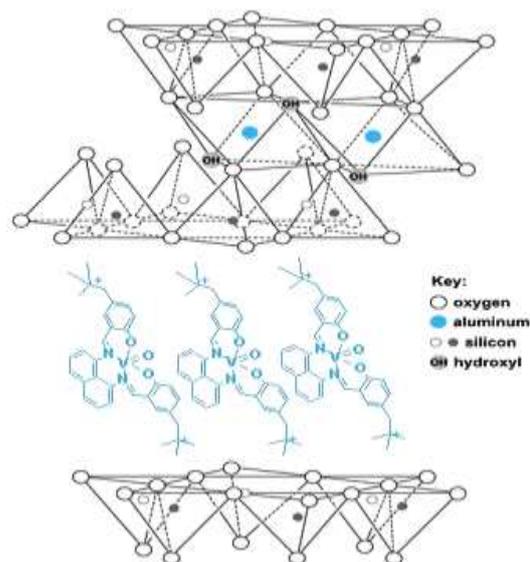
To a vigorously stirred ethanolic solution (40 mL) of 3-formyl-4-hydroxy benzyltriphenyl phosphonium chloride (0.864 g, 2 mmol) was added dropwise a solution of 1,8-naphthal-diamine (0.158 g, 1 mmol) in 30 mL of ethanol. After the addition was complete, the mixture was stirred and refluxed for 8 hr. The solvent was partially removed under reduced pressure on a rotary evaporator, and the yellow product was precipitated by n-hexane. The schiff base ligand was filtered and dried in vacuum.(yield 0.9 g, 91%). Anal. Calcd for C₆₂H₅₀N₂P₂O₂Cl₂(%) : C, 75.38; H, 5.10; N, 2.84. Found: C,75.5; H, 5.2; N, 2.51. d. p.: >400°C. IR (KBr, cm⁻¹): 1604 [ν (C=N)], 3437 [ν (O-H)]. ¹HNMR (500MHz, CDCl₃):12.2 (s, 2H, OH),8.1 (s, 2H, Ar-CH=N), 6.8-7.8 (m, 42H, Ar), 4.2 (s, 4H, Alkane).

2.4 Synthesis of schiff base complex

To 60 mL of an ethanolic solution of $\text{VO}(\text{acac})_2$ (0.53 g, 2mmol) was added the ethanolic solution (20 mL) of N, N'-bis{5-[(triphenylphosphoniumchloride)-methyl]salicylidine}-naphhtaldiamine (1.98 g, 2mmol). The yellow solution turned to dark green immediately and the mixture was vigorously stirred and refluxed for 120min. The dark green powder was precipitated by n-hexane. Then the resulting powder precipitate was collected by filtration, washed with ethanol and ether and dried in air. (yield 1.37 g, 65 %). Anal. Calcd for $\text{C}_{62}\text{H}_{48}\text{N}_2\text{P}_2\text{O}_3\text{Cl}_2\text{V}$ (%) : C, 70.6; H, 4.57; N, 2.67. Found: C, 70.2; H, 4.32; N, 2.91. d.p.: $>400^\circ\text{C}$. IR (KBr, cm^{-1}): 1594 [$\nu(\text{C}=\text{N})$]. DRS [$d \rightarrow d$ (nm)]: 350, 455. Molar conductance [$\Omega^{-1}\text{cm}^2 \text{mole}^{-1}$]: 275 in acetonitrile.

2.5 Immobilization of Vanadyl Schiff base on sodium montmorillonite

$\text{VO}(\text{Schiff base})$ complex (1.0 g) was dissolved in 20 mL hot methanol and was slowly added to 1 g of sodium montmorillonite in 40 mL methanol. The mixture was heated and stirred for 24 h under inert atmosphere. The resultant hot mixture was filtered and washed with hot methanol then was Soxhlet extracted with a mixture of 1:1 methanol and acetone in order to remove unreacted $\text{VO}(\text{Schiff base})$ complex (Scheme 1). The resultant powder was filtered and washed with hot methanol and dried at 60°C under vacuum. Anal. Found for catalyst(%): C, 19.32; H, 2.32; N, 0.78; C/N, 24.76 [calcd. C/N for net $\text{VO}(\text{Schiff base})$ complex: 24.1]; %V (Atomic absorption): 1.31; IR (KBr, cm^{-1}): 1596 [$\nu(\text{C}=\text{N})$]; DRS [$d \rightarrow d$ (nm)]: 350, 456



Scheme 1. Preparation of heterogeneous catalyst

2.6 Epoxidation of olefins by heterogeneous catalyst

Epoxidation of olefins such as cyclooctene, cyclohexene, styrene, indene, α -pinene and 1-octene using homogeneous and heterogeneous form of catalyst was carried out in a 25 mL Schlenk tube. All glasswares were oven-dried prior to use. The system was purged with argon gas. In a typical experiment, a mixture of 0.2 g of $\text{VO}(\text{Schiff base})@mont$, (5.14×10^{-5} mol for net complex), and freshly distilled acetonitrile (10 mL), 10 mmol freshly distilled olefin and 15 mmol of TBHP was refluxed for 8 h. The reaction was quenched by addition of excess triphenylphosphine to destroy remaining peroxide. After filtration (heterogeneous catalysts), the solid was washed with acetonitrile. The filtrate was then injected to GC analysis. Internal standard 1,2-dichlorobenzene was used for olefins.

3. Results and Discussion

3.1 Characterization of ligand, vanadyl Schiff base complex and heterogeneous catalysts

Tetradentate Schiff base ligand was obtained by the reaction of 1,8-naphhtaldiamine with two equivalents of formyl-4-hydroxy benzyltriphenyl phosphonium chloride. The vanadyl- N, N'-bis(5-[(triphenylphosphoniumchloride)-methyl-salicylidene]naphhtaldiamine) was prepared by the reaction of Schiff base ligand with an equivalent of $\text{VO}(\text{acac})_2$. The molar

conductance values of neat complex ($275 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$) was measured in acetonitrile corresponds to 1:2 electrolytes [28]. The IR spectra of Schiff base ligand and vanadyl complex (Figure 1) shows C=N stretching vibrations at 1604 and 1594 cm^{-1} , respectively which shift approximately 10 cm^{-1} to lower wavenumbers upon coordination. The IR spectra of heterogeneous catalyst at 1596 cm^{-1} is assigned to C=N stretching vibrations of complex. The slightly (2 cm^{-1}) difference in their wavenumbers of C=N stretching vibrations of *VO(Schiff base)@mont* and VO(Schiff base) shows that the complex is physically entrapped within the clay. The diffuse reflectance spectra (DRS) bands of *VO(Schiff base)* at, 350 and 455 nm can be attributed to ${}^2B_2 \rightarrow {}^2E$ and ${}^2B_2 \rightarrow {}^2B_1$ transitions [29]. The comparison of diffuse reflectance spectrum (DRS) of the heterogeneous VO(Schiff base)@mont catalyst and vanadyl Schiff base complex (Figure 2) show that the vanadyl complex was physically entrapped within the sodium montmorillonite clay. The immobilization process was characterized by the change of color of the clays from light cream to light green. The suspension were filtered and washed with methanol and dried in desiccator. The heterogeneous catalyst was very stable in common organic solvents as methanol, dichloromethane, acetonitrile and water as they released no vanadyl Schiff base complex even after stirring in the solvents for several days. The molecular formulae of the vanadyl Schiff base complex have been assigned on the basis of the results of their elemental analyses. The chemical composition was confirmed the purity and stoichiometry of the neat and entrapped complexes. The vanadium content of the VO(Schiff base)@mont catalyst and neat complex was estimated using atomic absorption spectroscopy (AAS). The chemical analysis of the heterogeneous catalyst reveals the presence of organic matter with a C/N ratio roughly similar to neat vanadyl Schiff base complex.

Figure 3 depicts the powder small angle X-ray diffraction pattern of the Na-montmorillonite clay and basal spacing d_{001} of VO-Schiff base complex pillared montmorillonite. The basal spacing (d_{001}) of VO(Schiff

base)@mont product is about 1.78 nm. Since the thickness of a montmorillonite crystal layer is about 0.96 nm. Comparison of the basal spacing of Na-montmorillonite with VO(Schiff base)@mont indicates that the VO-Schiff base complex was fixed into the interlayer of montmorillonite. Figure 4 shows the morphology of clay-supported vanadyl complex that was observed by SEM.

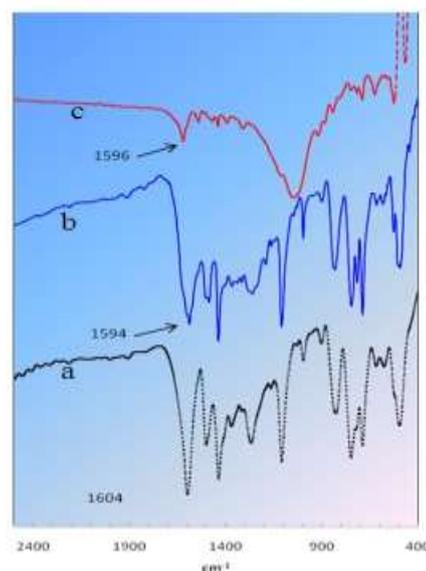


Fig. 1. FT-IR spectrum of (a) ligand, (b) Vanadyl Schiff base complex, (c) Vanadyl Schiff base complex@Mont

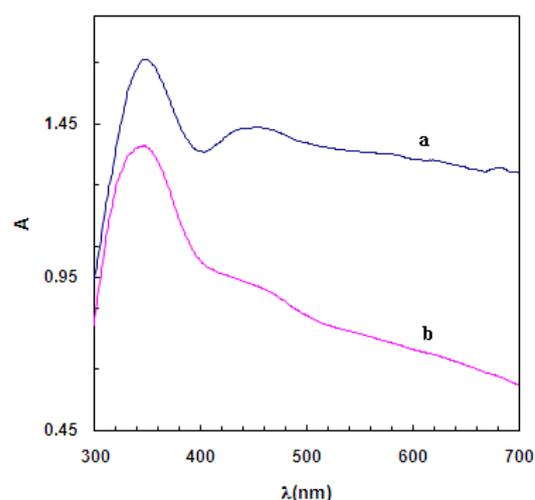


Fig. 2. DRS spectrum of (a) Vanadyl Schiff base complex, (b) Vanadyl Schiff base complex@Mont

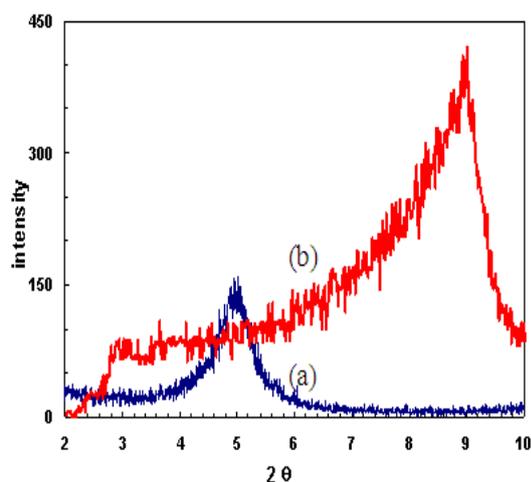


Fig. 3. Small angle X-ray diffraction pattern of (a) Vanadyl Schiff base complex@Mont and (b) Na-montmorillonite

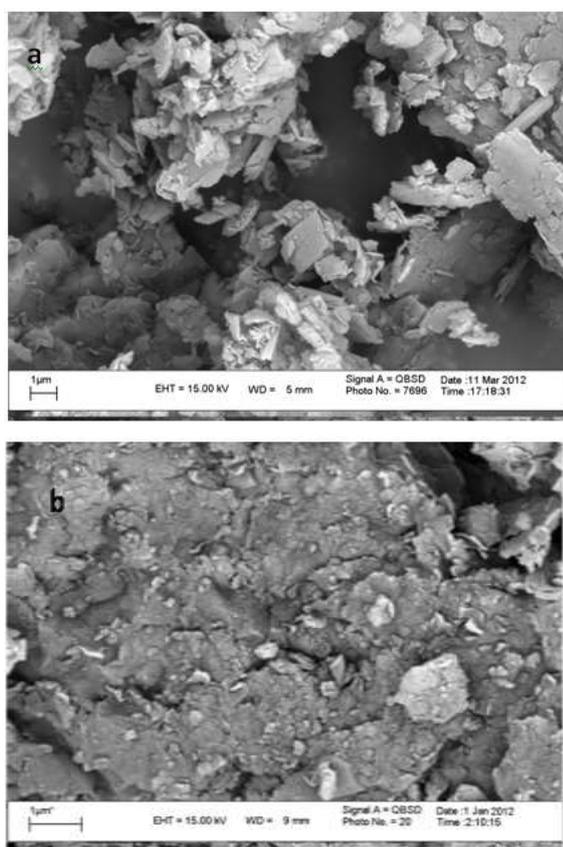


Fig. 4. Scanning electron micrograph of: (a) Vanadyl Schiff base complex@Mont (b) Na-montmorillonite

3.2 Catalytic epoxidation of olefins

The catalytic reactivity of heterogeneous and homogeneous Oxovanadium(IV) Schiff base catalysts were tested for epoxidation of Cyclooctene,

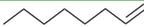
cyclohexene, styrene, indene, α -pinene and 1-octene. The conversion increases with increasing the reaction time. Conversion does not increase significantly after 8 h (Fig.5). The percent of conversion increased with increasing the molar ratio of [TBHP]: [cyclooctene] from 0.5 to 1.5 and decreased from 1.5 to 2.0. The conversion of cyclooctene was maximized at 1.5 molar ratio of [TBHP]: [cyclooctene] (Fig.6). The epoxidation of cyclooctene was carried out in toluene, dichloromethane, acetonitrile, dichloroethane and methanol in order to choose a suitable solvent. Our results showed acetonitrile was generally the best of the solvents tested in terms of yields during 8 h (Fig. 5). The effect of reaction temperature on conversion of cyclooctene was studied by varying the temperature in freshly distilled acetonitrile (10 mL), 10 mmol freshly distilled cyclooctene, 15 mmol of TBHP and 5.14×10^{-5} mol catalyst. The conversion increased with increasing the reaction temperature from 25°C to 80°C (Fig. 7). Hence, typical catalytic reaction conditions involve acetonitrile (10 mL) solutions at 78 ± 2 °C, olefin (10 mmol), TBHP (150 mmol) and catalyst (5.14×10^{-5} mol) stirred for 8 hrs. The final solution exhibited no color. So, no presence of metal was detected in the solution after using heterogeneous catalyst, (It was confirmed by atomic absorption spectroscopy). The product distributions in the oxidation of olefins using homogeneous and heterogeneous catalysts are shown in Tables 1. One of the main problems of homogeneous transition metal complexes as catalysts is the formation of oxo and peroxy dimeric and other polymeric species. The formation of these compounds can deactivate catalysts irreversibly. This problem may be solved by immobilizing of the metal complexes within the solid supports so it can separate complexes from each other. Then the dimeric and polymeric species will not form because of steric effect in this kind of heterogeneous catalysts. Results in table 1 appear that VO(Schiff base)@mont gave higher percent of conversion of olefins than neat vanadyl Schiff base complex. The cyclohexene oxidation proceeds with a moderate 100% selectivity for epoxidation with 91% conversion for

VO(Schiff base)@mont. Catalytic reactions were not affected by the presence or absence of light. The catalytic oxidation of cyclohexene with TBHP in the absence of catalysts or in the presence of neat clay, (15-20%) oxidation occurs with low conversion.

In the case of α -pinene, the major product is α -pinene oxide (70%), and allylic oxidation products, Verbenone (13%) and Verbenol (17%) were produced as minor products. The most important advantage of the heterogeneous VO(Schiff base)@mont catalyst is a high increasing of the complex stability in the reaction media and the possibility of easy reusing of the catalyst after reaction by simple filtration. The stability of vanadyl Schiff base supported in sodium montmorillonite was studied in repeated epoxidation reactions. After the use of catalyst for four consecutive times, the catalytic activity and selectivity of VO(Schiff base)@mont have not changed significantly (Table 1). The catalyst can be reused after washing with CH_2Cl_2 and drying under vacuum at 80 °C.

The observed result confirms that in the first step, mechanism involve the oxidation of vanadium(IV) Schiff base complex with TBHP and the interaction of it with TBHP to give vanadium(V) species [30]. In the next step, the mechanism involves the transfer of a TBHP proton to the terminal oxygen atom of one of the Vanadyl group and coordination of $t\text{-BuOO}^-$ to vanadium (V) as a Lewis acidic metal center and formation of the oxoperoxovanadium(V) intermediate.

Table 1. Results of catalytic epoxidation of olefins with TBHP catalyzed by Heterogeneous and Homogeneous vanadyl complex, acetonitrile =10 ml; catalyst= 5.14×10^{-5} mol; duration=8 h at reflux; olefin =10 mmol; TBHP=15 mmol

Entry	Alkene	%Conversion		% Epoxy		TON ^a	
		Heterogeneous (Homogeneous)	Heterogeneous (Homogeneous)	Heterogeneous (Homogeneous)	Heterogeneous (Homogeneous)	Heterogeneous (Homogeneous)	Heterogeneous (Homogeneous)
1		77 (72)	100 (100)	312(292)			
2		47 (41)	100 (100)	191(166)			
3		90 ^b (56)	100 (100)	365(227)			
		88 ^c	100				
		86 ^d	100				
		85 ^e	100				

In the homogeneous medium, Vanadium complex can further react, ultimately forming oxo dimeric specie [25]. It seems that the approach of cyclohexene to the metal center take place faster than the others.

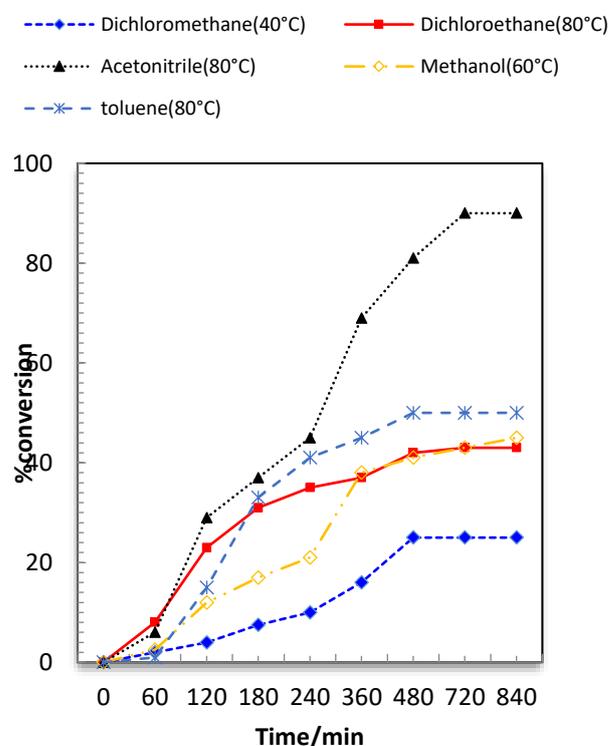
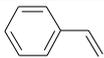


Fig. 5. Effect of reaction time on catalytic epoxidation of cyclooctene , acetonitrile =10 ml; catalyst= 5.14×10^{-5} mol at reflux; cyclooctene=10 mmol; TBHP=15 mmol

4		68 (60)	75 ^f (67)	276(243)
5		45 (38)	70 ^g (39)	183(154)
6		91 (72)	100 (100)	369(292)

a: TON: [The mole of olefin][conversion] / [mole of catalyst][min]

b: Reuse for second run

c: Reuse for third run

e: Reuse for fourth run

f: The by-product is 25% benzaldehyde for heterogeneous system and 33% for homogeneous system

g: The by-products are 13% verbenone and 17% verbenol for heterogeneous system and 24% verbenone and 37% verbenol for homogeneous system

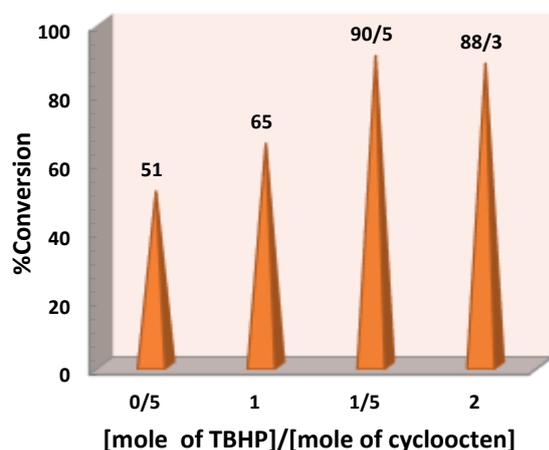


Fig 6. Effect of [TBHP]/ [cyclooctene] ratio on cyclooctene conversion at 80 °C

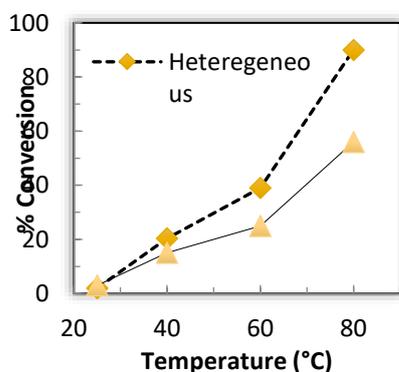


Fig. 7. The effect of reaction temperature on conversion of cyclooctene, acetonitrile =10 ml; catalyst= 5.14×10^{-5} mol at reflux; cyclooctene=10 mmol; TBHP=15 mmol

4. Conclusions

In the presented research, as a part of our progressing studies on the catalyst, we demonstrated the synthesis and characterization of new heterogeneous catalyst that have been prepared by immobilization of N_2O_2 type tetradentate Schiff base complex of Oxovanadium(IV) in to pillared sodium montmorillonite clay matrix. The IR, SEM, XRD and DRS data show that the vanadyl complex is physically supported throughout the matrix. The catalyst which can be easily prepared is heterogeneous and efficient chemoselective catalyst for epoxidation of alkenes such as cyclooctene, cyclohexene, styrene, indene, α -pinene, 1-octene using *tert*-butyl hydroperoxide with TBHP as oxygen source in acetonitrile. The reusability of catalyst is satisfying and can be reused four times without significant decrease in catalytic activity

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