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ORIGINAL PAPER

# Green oxidation of olefins and methyl phenyl sulfide with hydrogen peroxide catalyzed by an oxovanadium(IV) Schiff base complex encapsulated in the nanopores of zeolite-Y

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**Abstract** Oxovanadium(IV) complex of a Schiff base ligand derived from 2,4-dihydroxyacetophenone and 2,2′-dimethylpropanediamine has been encapsulated in the nanopores of zeolite-Y by flexible ligand method and characterized by metal analysis, IR spectroscopic studies and X-ray diffraction patterns. The encapsulated complex [VOL-Y] catalyzes the oxidation of various olefins and methyl phenyl sulfide using hydrogen peroxide as a green oxidant in good yield. Under the optimized reaction conditions, in the presence of VOL-Y, 86 % conversion of cyclooctene with 100 % selectivity for epoxide and 51 % conversion for methyl phenyl sulfide with 92 % selectivity for sulfone were obtained.

**Keywords** Heterogeneous catalyst · Zeolite · Schiff base · Oxidation · Alkene · Sulfide

## Introduction

Vanadium has been found to play a number of roles in biological systems. For example vanadium complexes are present in the haloperoxidases [1–3] where these complexes catalyze the oxidative halogenation of aromatic substrates using $H_2O_2$ as oxidant [4–7] or vanadium-based drugs that lower glucose [8–10] by enhancing the effects of insulin. Therefore, the study of vanadium compounds has long been of interest to chemists.

In the catalytic reactions, heterogenization of the homogeneous catalysts is a suitable method to achieve the higher activity, selectivity, and reusability of the catalysts. Therefore, heterogenization may be done by immobilization through covalent bonding on the functionalized MCM-41, SBA-15, etc. [11–18] or encapsulation in the nanocavity of, e.g. zeolites [19–21]. Recently, metal complexes encapsulated in the nanocavity of zeolite-Y have been widely used for many catalytic reactions such as the selective oxidation, alkylation, dehydrogenation, cyclization, amination, acylation, isomerization and rearrangement of various substrates and are able to produce intermediates as well as most industrial products [22–25].

In this work, we have encapsulated the dioxovanadium(IV) complex of a Schiff base ligand in the nanocavity of zeolite-Y and the catalytic activity of the heterogeneous catalyst in the oxidation of various olefins and methyl phenyl sulfide with hydrogen peroxide as a green oxidant has been investigated.

## Experimental

### Materials and physical measurements

Infrared spectra were recorded as KBr pellets using Unicam Matson 1000 FT-IR. A Varian (AA240) atomic absorption spectrometer was used for vanadium determination. $^1$H NMR spectrum was obtained in $CDCl_3$ with a Bruker FT-NMR 500 (500 MHz) spectrometer. The residual $CHCl_3$ in conventional 99.8 % $CDCl_3$ gives a signal at $\delta$ 7.26 ppm and was used for calibration of the chemical shift scale. Gas chromatography (GC) analyses were conducted on a Shimadzu chromatograph (model GC-14B) equipped with flame ionization detector and capillary

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column SAB-5 (phenyl methyl siloxane 30 m × 320 mm × 0.25 mm). Elemental analysis was performed using a CHN Perkin Elmer 2400 Series II.

2,2′-Dimethylpropylenediamine, 2,4-dihydroxyacetophenone, Na-Y zeolite, vanadyl acetylacetonate, methyl phenyl sulfide and hydrogen peroxide (30 % in $H_2O$) were used as received from commercial suppliers. The solvents were dried and distilled using standard methods before being used. Other chemicals were purchased from Merck or Fluka chemical companies.

### Preparation of the ligands ($H_2L$)

To a stirred ethanolic solution (30 mL) of 2,2′-dimethylpropelenediamin (0.102 g, 1 mmol), 2,4-dihydroxyacetophenone (0.304 g, 2 mmol) was added. The solution was stirred and heated to reflux for 1 h. An orange precipitate was obtained that was filtered off and washed with warm ethanol. Yield (90 %), Mp 120 °C. Anal. Calc. for $C_{21}H_{26}N_2O_4$ (370.44): C, 68.08; H, 7.07; N, 7.56. Found: C, 68.72; H, 7.53; N, 7.22 %. Selected FT-IR data, $\upsilon$ ($cm^{-1}$): 3,445(O–H), 2,972 (C–H), 1,612 (C=N), 1,504 (C=C), 1,057 (C–O). $^1H$ NMR ($\delta$/ppm):1.04 (s, 6H, $NCH_2C(\mathit{CH_3})_2CH_2N$), 2.26 (s, 6H, $\mathit{CH_3}C{=}N$), 3.42 (s, 4H, $N\mathit{CH_2}C(CH_3)_2\mathit{CH_2}N$), 6.05–7.39(m, 6H, ArH), 9.70 (br, 2H, ArOH), 17.01(s, 2H, ArOH).

### Preparation of oxovanadium(IV) complex

The complex was prepared by a general procedure: the ligand, $H_2L$ (0.37 g, 1 mmol), was dissolved in 20 mL of ethanol. An ethanolic solution of vanadyl acetylacetonate (0.265 g, 1 mmol) was added to above solution and the reaction mixture was refluxed for 1 h. The colored solution was concentrated to yield colored powders. The products were washed with warm ethanol. General structure of oxovanadium(IV) complexes is shown in Fig. 1. Yield (72 %), Dp 290 °C. Anal. Calc. for $C_{21}H_{24}N_2O_5V$ (435.37): C, 57.93; H, 5.55; N, 6.43. Found: C, 57.65; H, 5.73; N, 6.56 %. Selected FT-IR data, $\upsilon$ ($cm^{-1}$): 2,962 (C–H), 1,605 (C=N), 1,540 (C=C), 1,057 (C–O).

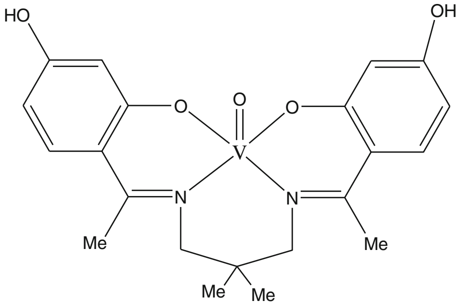


**Fig. 1** General structure of oxovanadium(IV) complex

### Incorporation of oxovanadium(IV) in Na-Y (metal exchanged Y-zeolite)

5 g Na-Y zeolite was suspended in 100 mL distilled water containing vanadyl acetylacetonate (12 mmol). The mixture was then stirrer for 24 h. The solid was filtered and washed with deionized water and dried at room temperature to give the light-green powder of VO-Y (Scheme 1, **I**).

### Immobilization of $H_2L$ in VO-Y

An amount of 1.0 g VO(IV)-Y and 2.5 g of ligand $H_2L$ were mixed in 100 mL of methanol and the reaction mixture was refluxed for 15 h in an oil bath with stirring. The resulting material was separated by filtration and then extracted with methanol using Soxhlet extractor to remove unreacted ligand from the cavities of the zeolite as well as those located on the surface of the zeolite along with neat complexes, if any. The unreacted oxovanadium(IV) ions present in the zeolite was removed by stirring with aqueous 0.01 M NaCl solution. The resulting solid was filtered and washed with distilled water until free from chloride ions. Finally, it was dried at 120 °C in an air oven for several hours.

### General oxidation procedure

Catalytic experiments were carried out in a 10-mL glass reaction flask fitted with a water condenser. In a typical reaction, alkene (0.2 mmol) and catalyst (1 mg) were mixed in 1 mL of $CH_3CN$ and hydrogen peroxide (1 mL) was added to it and the reaction mixture was heated in an oil bath for 4 h. The reaction products were analyzed using a gas chromatograph after a specific interval of time by withdrawing a small aliquot of reaction mixture.

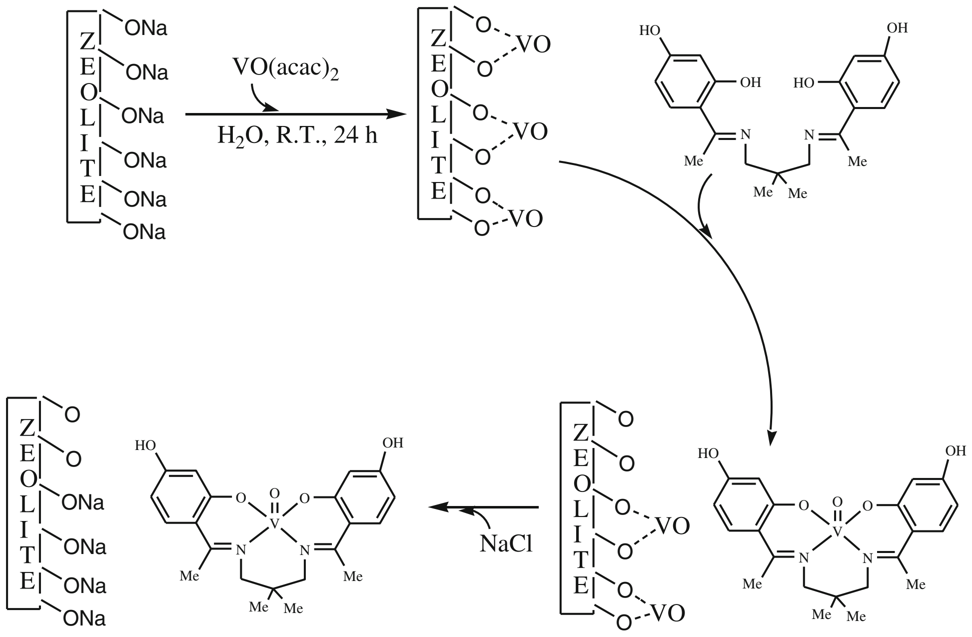
## Results and discussion

### Characterization of oxovanadium complex encapsulated in the zeolite-Y

#### *IR spectral studies*

A sharp band appearing at 1,612 $cm^{-1}$ due to $\nu$(C=N) in the $H_2L$ (azomethine) shifts to lower wave numbers and appears at 1,605 $cm^{-1}$ in the VOL. This indicates the involvement of azomethine nitrogen in coordination to the vanadium center. Also, $\nu$(C=N) of VOL-Y appears at frequencies shifted 6 $cm^{-1}$ (1,599 $cm^{-1}$) from those of the

**Scheme 1** Encapsulation of the oxovanadium(IV) complex in the nanopores of zeolite-Y



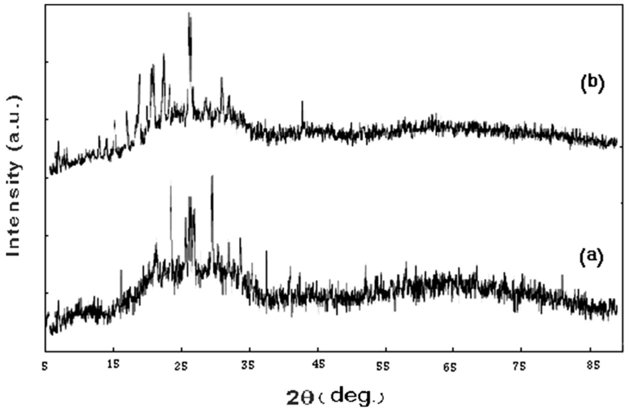


**Fig. 2** XRD patterns of VO-Y (*a*) and VOL-Y (*b*)

free complex [VOL]. On the other hand, neat complex [VOL] exhibits a sharp band at 846 cm$^{-1}$ due to the $v$(V=O) stretch [26], while in zeolite encapsulated vanadium complex $v$(V=O) stretch appears at 846 cm$^{-1}$. These observations not only confirm the presence of [VOL] in the zeolite, but also suggest that its structure is almost identical to that of the free complex. The spectra of Na-Y and VO-Y show a broad band in the range 3300–3700 cm$^{-1}$ due to surface hydroxylic groups and lattice vibrations at ca. 1,000 cm$^{-1}$.

### *Powder X-ray diffraction studies*

The powder X-ray diffraction patterns of VO-Y and VOL-Y (Fig. 2) were recorded at 2$\theta$ values between 5° and 90°. The XRD patterns of VO-Y is similar to that of VOL-Y and a slight change in the intensity of the bands shows that the zeolite crystallinity is retained on encapsulating complex. This observation confirms that the framework of the zeolite has not undergone any significant structural change during encapsulation.

### *The catalytic oxidation of alkenes*

The catalytic performance of VOL-Y in the oxidation of cyclooctene, as a model substrate, and hydrogen peroxide as the source of oxygen was investigated. A series of blank experiments (Table 1) show that the presence of catalyst and oxidant is essential for an effective catalytic reaction.

The results in Table 1 show that oxidation of cyclooctene needed 1 mL of $H_2O_2$ for completion.

To find the optimum reaction conditions, the effect of various reaction parameters that may affect the conversion and selectivity of the reaction was investigated. Solvent, catalyst concentration, reaction time and amount of the oxidant are the factors that have been evaluated.

The influence of the solvent nature in the catalytic activity of the VOL-Y for epoxidation of cyclooctene has been studied. Therefore, chloroform, acetonitrile, dichloromethane, methanol and ethanol were used and the highest conversion was obtained in acetonitrile (Table 2).

The higher conversions in acetonitrile (86 %) relative to the others possibly may be due to the higher boiling point of acetonitrile.

The effect of reaction time in the catalytic epoxidation of cyclooctene with $H_2O_2$ in the presence of VOL-Y is shown in the Fig. 3 and the highest conversion (100 %) was obtained after 5 h.

**Table 1** Catalytic oxidation of 0.2 mmol cyclooctene with $H_2O_2$ in the presence of VOL-Y in acetonitrile under reflux condition

| Catalyst | $H_2O_2$ | Conversion (%) | Selectivity (%) (Epoxide) |
|---|---|---|---|
| VOL-Y | – | 0 | – |
| None | 0.6 mmol | 0 | – |
| 1 mg | 0.6 mmol | 9 | 100 |
| 1 mg | 1 mL | 86 | 100 |

**Table 2** The catalytic epoxidation of cyclooctene in different solvents

| Solvent | Boiling point(°C) | Dielectric constants | Conversion (%) |
|---|---|---|---|
| Dichloromethane | 40 | 8.9 | 0 |
| Chloroform | 61 | 4.9 | 0 |
| Methanol | 64 | 32.7 | 20 |
| Ethanol | 78 | 26.6 | 29 |
| Acetonitrile | 81 | 37.5 | 86 |

Reaction conditions: (0.2 mmol) cyclooctene, (1 mL) $H_2O_2$, (4 h) reaction time, (1 mg) VOL-Y

Different catalyst concentrations have been used in the oxidation of cyclooctene (Table 3). It was observed that oxidation of cyclooctene required 0.015 g of catalyst for completion.

To establish the general applicability of the method, under the optimized conditions, oxidation of various olefins was subjected in the presence of the catalytic amount of VOL-Y and the results are presented in Table 4.

Comparison of the catalytic behavior of the oxovanadium Schiff base complex encapsulated onto nanopores of zeolite-Y and free VOL (Table 5) showed the higher catalytic activity of the heterogeneous catalyst with respect to the homogenous one.

**Table 3** The influence of catalyst VOL-Y concentration on the catalytic epoxidation of cyclooctene with $H_2O_2$ under reflux condition

| VOL-Y(mg) | Catalyst:substrate (mol % cat. = 4.1) | Conversion (%) | Selectivity (%) (Epoxide) |
|---|---|---|---|
| 0.8 | 1:300 | 46 | 100 |
| 1 | 1:250 | 86 | 100 |
| 1.2 | 1:200 | 26 | 100 |

Reaction conditions: (1 mL) $CH_3CN$, (0.2 mmol) cyclooctene, (1 mL) $H_2O_2$, 4 h (time)

The ease of separation is one of the greatest advantages of heterogeneous catalyst while the homogeneous vanadium complex cannot be recovered even once. Therefore, reusability of the heterogeneous catalyst VOL-Y was studied and results showed that the VOL-Y can be separated from reaction mixture, washed with solvent and dried before being used. The catalyst was consecutively reused six times without a detectable catalyst leaching or a significant loss of its activity.

In a proposed catalytic cycle, hydrogen peroxide will be activated by coordination to the oxovanadium(IV) center and then nucleophilic attack of olefin on the electrophilic oxygen atom covalently bonded to the metal leading to the formation of epoxide product (Scheme 2) [27–29].

## Catalytic oxidation of methyl phenyl sulfide

Oxidation of methyl phenyl sulfide with hydrogen peroxide catalyzed by VOL-Y gave methyl phenyl sulfone as the major product. In a search for suitable reaction conditions to achieve the maximum conversion, the effect of different parameters including solvent, temperature, amount of oxidant and the presence of acetic acid (HOAc) as oxidant activator was studied.

The results for the oxidation of methyl phenyl sulfide show that after 120 min (Table 6), only 25 % methyl phenyl sulfide conversion was obtained. Therefore, hydrogen peroxide can be activated by addition of acetic acid (HOAc).

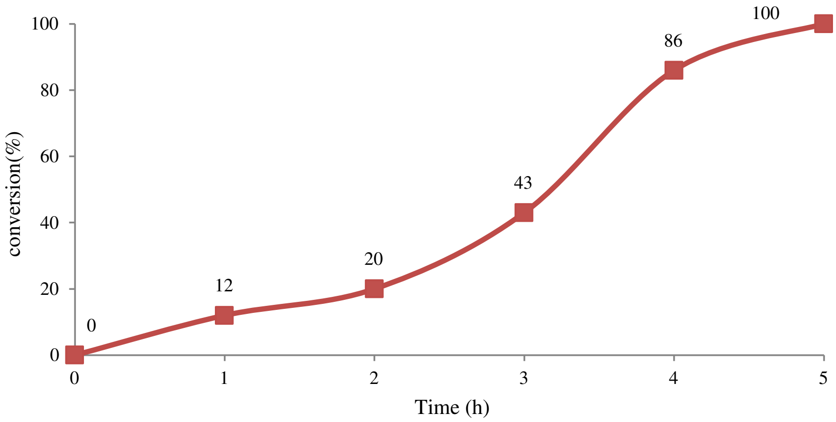
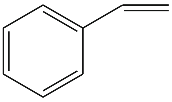
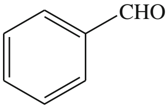
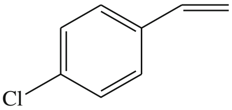
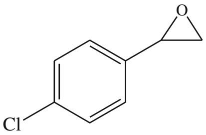
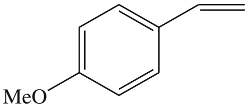
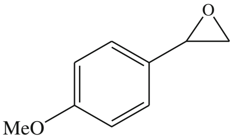
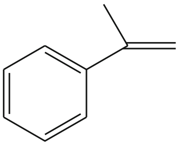
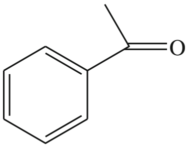
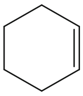
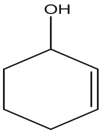
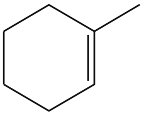
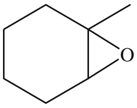
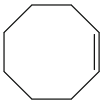
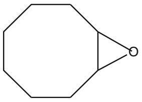


**Fig. 3** The effect of reaction time in the oxidation of cyclooctene with $H_2O_2$ in the presence of VOL-Y. Reaction conditions: (1 mL) $CH_3CN$, (0.2 mmol) cyclooctene, (1 mL) $H_2O_2$, (1 mg) VOL-Y

**Table 4** Oxidation of olefins using $H_2O_2$ catalyzed by VOL-Y in $CH_3CN$

| Alkene | Conversion (%)[a] | Product | Selectivity (%) | TON[e] (total) |
|---|---|---|---|---|
|  | 20 |  | 75[b] | 50 |
|  | 26 |  | 100 | 64 |
|  | 5 |  | 100 | 13 |
|  | 42 |  | 90[c] | 192 |
|  | 100 |  | 57[d] | 250 |
|  | 63 |  | 100 | 157 |
|  | 86 |  | 100 | 215 |
|  | 6 |  | 100 | 14 |

(0.2 mmol) alkene, (1 mL) $H_2O_2$, (1 mL) $CH_3CN$, (4 h) time

[a] Conversions and selectivities were determined by GC based on the starting alkene

[b, c, d] Epoxide was formed as by-product

[e] TON: (total turnover number) the ratio of the number of moles of product to the number of moles of catalyst

**Table 5** Comparison of homogeneous and heterogeneous systems

| Catalyst | Catalyst:alkene (mol % cat. = 4.1) | Conversion (%) | Selectivity epoxide (%) |
|---|---|---|---|
| VOL-Y | 1:250 | 86 | 100 |
| VOL | 1:250 | 61 | 100 |

Reaction conditions: (1 mL) solvent, (0.2 mmol) cyclooctene, (1 mL) $H_2O_2$

The amount of HOAc has been optimized and results presented in Table 7 show that the 51 % methyl phenyl sulfide conversion was obtained by addition of 80 µL HOAC.

To achieve the best reaction solvent, the reaction was performed in methanol, ethanol and acetonitrile and the highest conversion was achieved in ethanol as a more convenient and environmentally friendly solvent (Table 8).

Different catalyst concentrations have been used in the oxidation of methyl phenyl sulfide (Fig. 4) and the highest conversion was achieved with 6 mg of heterogenous catalyst.

In the absence of catalyst, the oxidation of methyl phenyl sulfide with hydrogen peroxide did not proceed even after 45 min. Also, in the presence of acetic acid a conversion of 14 % was obtained. These observations suggest a catalytic cycle containing heterogeneous catalyst and peracetic acid formed by the reaction of hydrogen peroxide and HOAc [30] as oxidant. Increasing the rate of the reaction by addition of HOAc suggests the formation of a peracetic acid species that will be activated under surface of the catalyst (Scheme 3).

## Conclusion

In conclusion we have reported the synthesis and characterization of an oxovanadium(IV) Schiff base complex encapsulated in the nanopores of zeolite-Y. Also, this heterogeneous catalyst has been used for oxidation of different alkenes and methyl phenyl sulfide with hydrogen

**Scheme 2** Proposed catalytic cycle for oxidation of alkenes

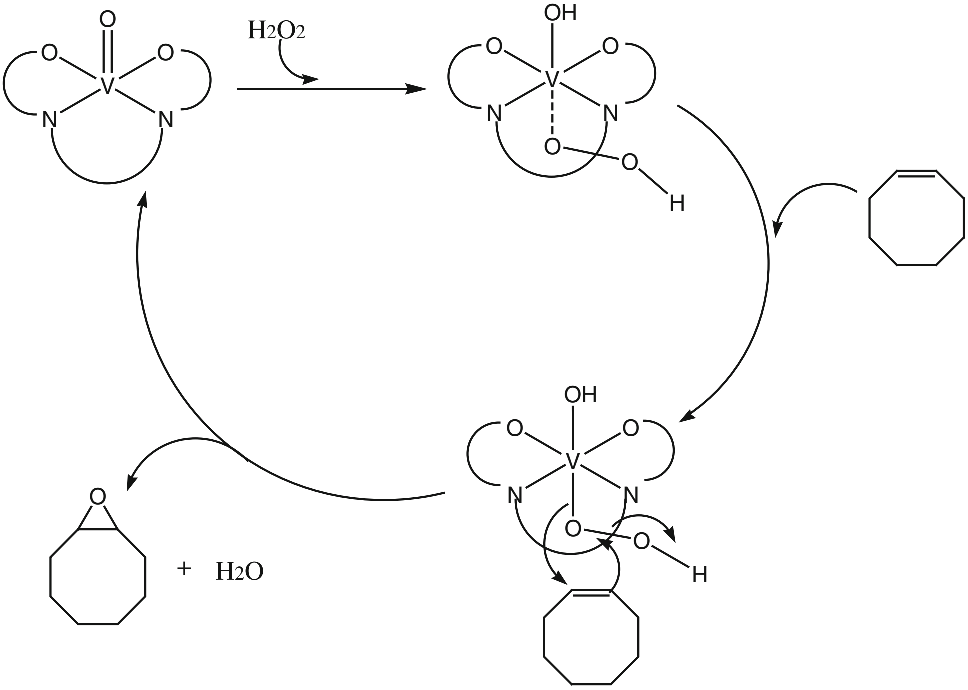


**Table 6** Catalytic oxidation of methyl phenyl sulfide in the presence of 6 mg of VOL-Y in ethanol at room temperature

| Conversion (%) | Selectivity (%) Sulfone | Time (min) |
|---|---|---|
| 12 | 100 | 30 |
| 25 | 100 | 120 |

**Table 7** The effect of acetic acid concentration on the oxidation of methyl phenyl sulfide catalyzed by VOL-Y in ethanol at room temperature

| Acetic acid (μL) | Conversion (%) | Selectivity (%) Sulfone |
|---|---|---|
| 40 | 26 | 100 |
| 80 | 51 | 92 |
| 100 | 5 | 100 |

Reaction conditions: (1 mL) solvent, (0.2 mmol) cyclooctene, (1 mL) $H_2O_2$

**Table 8** The effect of solvent on the oxidation of methyl phenyl sulfide

| Solvent | Conversion (%) | Selectivity (%) (Sulfone) |
|---|---|---|
| Methanol | 23 | 70 |
| Acetonitrile | 5 | 100 |
| Ethanol | 51 | 92 |

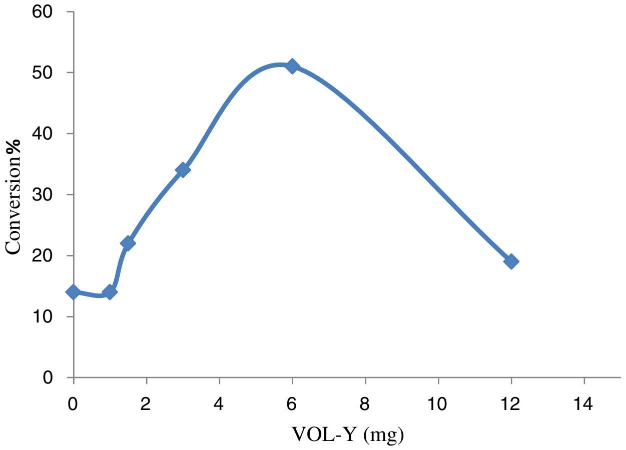
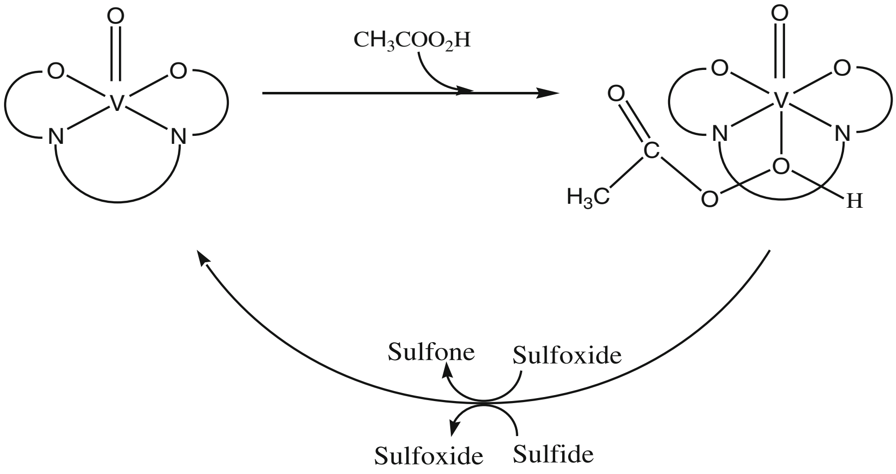


**Fig. 4** The effect of catalyst concentrations on the oxidation of methyl phenyl sulfide

peroxide. Different reaction parameters were investigated and optimized in the oxidation reaction. The results showed that the vanadyl complex was active and highly selective in the oxidation of olefins. In addition, catalytic oxidation of methyl phenyl sulfide with activated hydrogen peroxide by acetic acid gave methyl phenyl sulfone as the major product.

**Scheme 3** Proposed catalytic cycle for oxidation of methyl phenyl sulfide



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