# Oxo-Vanadium(IV) Dihydrogen Phosphate: Preparation, Magnetic Study, and Heterogeneous Catalytic Epoxidation

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A layered oxo-vanadium(IV) dihydrogen phosphate, $\{VO(H_2PO_4)_2\}_n$ has been synthesized hydrothermally and characterized by several physicochemical methods. Single-crystal X-ray analysis (crystal system, tetragonal; space group, *P4/ncc*; unit cell dimensions, $a = b = 8.9632(4)$, $c = 7.9768(32)$ Å) of $\{VO(H_2PO_4)_2\}_n$ reveals that the compound has an extended two-dimensional structure. The $VO^{2+}$ moieties are connected through bridging $H_2PO_4^-$ ions, and this type of connection propagates parallel to the crystallographic *ab* plane which gives rise to a layered structure. The layers are staked parallel to the crystallographic *c* axis with a separation between the layers of ca. 4.0 Å. Magnetic susceptibility of $\{VO(H_2PO_4)_2\}_n$ has been measured in the temperature range 2–300 K on a SQUID magnetometer. The magnetic property of $\{VO(H_2PO_4)_2\}_n$ is explicable in the light of a two-dimensional quantum Heisenberg antiferromagnet model. Magnetic pathways are available through the dihydrogen–phosphato bridges within the layer and provide for weak antiferromagnetic interactions. Notably $\{VO(H_2PO_4)_2\}_n$ catalyzes the epoxidation reaction of alkenes with *tert*-BuOOH in acetonitrile medium under heterogeneous condition.

## Introduction

Transition metal coordination polymers are increasingly attracting attention in recent time because of their fascinating molecular topologies and their application potential in developing new catalytic, magnetic, and fluorescent materials.[1,2] One of the most efficient methods for synthesizing such materials is hydrothermal assembly by incorporating desired metal ions with polydentate bridging ligands.[3] This method has been used extensively for the preparation of zeolites and mesoporous silica[4] and is now being used as an effective and routine technique for synthesizing inorganic coordination polymers in crystalline form. Vanadium phosphate and organophosphonates are a large class of compounds which have been studied in depth in recent times.[5,6]

Porous metal phosphates and amine-templated metal phosphates have received intense attention over the last few decades due to their application potential in catalysis, solid adsorbents, ion exchangers, etc.[7] A copious number of layered oxo-vanadium(V) phosphates and divalent metal incorporated oxo-vanadium(V) phosphates have been synthesized hydrothermally.[8–11]

Low-dimensional magnetism plays an important role in the understanding of phase transitions and critical phenomena; consequently, there has been enhanced interest in low-dimensional magnetism in condensed matter physics. In $La_2CuO_4$ type insulating superconductors with layers of $S = \frac{1}{2}$, Cu(II) ions have demonstrated the existence of strong antiferromagnetic interactions within the layers that have relevance to the critical temperature of the superconductor.[12] To understand the magnetic behavior of the two-dimensional (2D) $S = \frac{1}{2}$ (or quantum) Heisenberg antiferromagnet (2D QHAF) has led to a considerable amount of theoretical[13] and experimental study.[14–18] Numerous

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layered compounds containing Cu(II) ions have been synthesized, and their magnetic properties have been studied with respect of QHAF.[19,20] Although oxo-vanadium(IV) ($S = {}^1\!/_2$) is a good candidate to give rise to QHAF, reports on this system are very rare.[21] Recently Lumsden et al. reported that $K_2V_3O_8$, a 2D Heisenberg antiferromagnet, can be prepared by mixing $VO_2$ in a molten $KVO_3$.[21] Upon cooling, $K_2V_3O_8$ crystallizes in a tetragonal unit cell with $P_{4bm}$ space group. In $K_2V_3O_8$, a pyramidal V(IV)−$O_5$ moiety is surrounded by four tetrahedral nonmagnetic V(V)−$O_4$ moieties to form the layer, while $K^+$ ions occupy the interstitial sites of the crystal. Clearly, the layered oxo-vanadium(IV) system is worth trying to prepare new types of Heisenberg antiferromagnets.

There have been extensive studies on selective catalytic oxidation reactions of alkenes, alkanes, aromatics, alcohols, etc., using vanadium complexes as catalyst in heterogeneous or homogeneous medium.[22–24] The activity and selectivity of the vanadium oxide catalysts are mainly attributed to the changes in the oxidation state during the reaction. A lot of vanadium-based catalysts such as $VO(acac)_2$,[25] microencapsulated VO(a-cac)$_2$,[26] VO(Schiff-base),[27] silica-supported vanadium oxides,[28] vanadium aluminum phosphates (VAPO),[29] transition metal doped VPO,[30] etc., have been used as oxidizing catalysts. Vanadium phosphates represent perhaps the best documented heterogeneous catalysts since their discovery as effective catalytic materials.[31,32] The oxo-vanadium phosphate system has been studied extensively for catalytic applications, most specifically the selective oxidation of butane to maleic anhydride by vanadyl pyrophosphate and vanadyl phosphite.[6a,33–36] This system exhibits considerable structural and compositional variety,[37] showing the variable oxidation states and coordination polyhedra accessible to the vanadium center, the ability of vanadium polyhedra to aggregate into oligomers or chain or network substructures, and the possibility of protonation of oxygen sites. Among vanadium phosphates, $VO(H_2PO_4)_2$ has been synthesized and characterized

structurally by Linde et al.[38] However, with regard to the catalytic efficacy, $\{VO(H_2PO_4)_2\}_n$ has not received much attention except for a few recent reports by Hutchings et al.[39] To our knowledge no attempts have been made so far to use oxo-vanadium(IV) phosphate catalysts in olefin epoxidation reactions.

Here we report the hydrothermal synthesis of layered $\{VO(H_2PO_4)_2\}_n$ along with its magnetic properties and catalytic activity toward epoxidation of alkenes using *tert*-BuOOH (TBHP) as oxidant.

## Experimental Section

**Materials.** Ammonium metavanadate, cyclohexene, cyclooctene, norbornene, styrene, *trans*-stilbene and TBHP (70% aqueous) were purchased from Aldrich and were used as received. Orthophosphoric acid (ca. 88%, density = 1.7) and solvents were purchased from Merck (India). The solvents were distilled and dried before use.

**Physical Measurements.** Fourier transformed infrared spectra of KBr pellets were measured on a Shimadzu S-8400 FTIR spectrometer. The vanadium content of the sample was estimated on a Varian Techtron AA-ABQ atomic absorption spectrometer. Magnetic measurements were carried out with a Quantum Design SQUID MPMS XL magnetometer. Diamagnetic corrections were estimated from the Pascal constants. The powder X-ray diffraction (XRD) patterns of the samples were recorded with a Scintag XDS-2000 diffractometer using Cu Kα radiation. The products of the catalytic reactions were identified and quantified by a Varian CP-3800 gas chromatograph using a CP-Sil 8 CB capillary column. $N_2$ sorption measurements were performed on a Belsorp-HP (Bel Japan Inc.) gas sorption system at 77 K. Prior to sorption experiments, samples were outgassed at desired temperature (100 °C) for ca. 8−9 h under vacuum ($10^{-3}$ Torr). The specific surface area $S_{BET}$ was determined by BET (Brunauer−Emmett−Teller) method. Other instruments used in this study were the same as reported earlier.[4d,40]

**Synthesis of $\{VO(H_2PO_4)_2\}_n$.** The phase pure compound was synthesized by hydrothermal treatment of ammonium metavanadate (0.12 g, 1 mmol) with large excess orthophosphoric acid (3.2 mL, 55 mmol) in the presence of ethylenediamine (0.36 g, 6 mmol) dissolved in 20 mL of milliQ water in a 250 mL Teflon-lined autoclave for 3 days at 160 °C followed by quenching the autoclave in cold water. Dazzling green needle-shaped crystals (yield 50%) were separated out during hydrothermal treatment. The crystals were filtered off by suction and washed with copious amount of distilled water and dried in air. Elemental analysis shows that compound $\{VO(H_2PO_4)_2\}_n$ contains 19.6% of vanadium (calcd 19.9%) and 1.6% of hydrogen (calcd 1.5%). The FTIR spectrum of $\{VO(H_2PO_4)_2\}_n$ shows two strong absorptions at 988 and 909 cm$^{-1}$ which are ascribable due to the terminal V=O stretching and V−O−V vibrations, respectively. Bands at 1107 and 1052 cm$^{-1}$ are assigned to $\nu$(P−O) vibrations. Notably the same compound, $\{VO(H_2PO_4)_2\}_n$ is obtained in this process when any aldehyde or ketone (e.g., octanal or octan-2-one) is used in lieu of ethylenediamine.

**Catalytic Reactions.** The catalytic reactions were carried out in a glass batch reactor according to the following procedure. Substrate, solvent, and catalysts were first mixed. The mixture was then equilibrated to 70 °C in an oil bath. After addition of TBHP, the reaction mixture was stirred continuously for 24 h. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified by gas chromatography and verified by GCMS.

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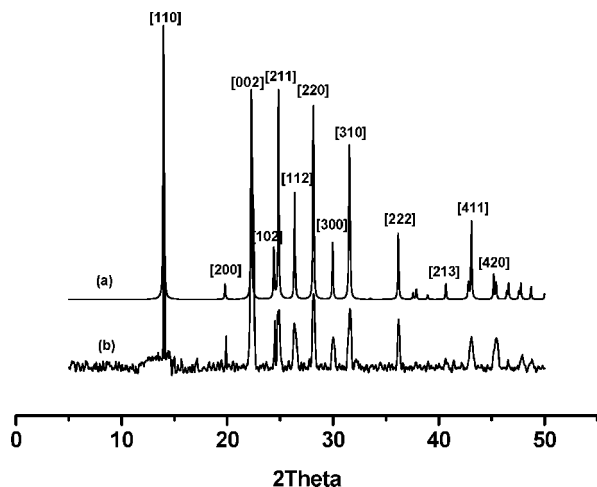
**Figure 1.** X-ray powder pattern of $\{VO(H_2PO_4)_2\}_n$ (calculated from single crystal data (a); experimental values (b)). Values given in the square brackets (curve a) are the indexing of the diffraction lines.

## Results and Discussion

**Synthesis of $\{VO(H_2PO_4)_2\}_n$.** In our attempts for synthesizing a new type of organic−inorganic hybrid material by hydrothermal process using ethylenediamine, ammonium metavanadate, and $H_3PO_4$, we observed that increasing in the molar ratio of $H_3PO_4$ to $(NH_4)VO_3$, there has been an increase in the amount of $\{VO(H_2PO_4)_2\}_n$ formed as a minor product, in addition to the usual products that are expected to form as reported earlier.[5,41] Subsequently addition of a large excess of $H_3PO_4$ ($(NH_4)VO_3$: $H_3PO_4 = 1:55$) into the reaction mixture yielded needle-shaped single crystals of $\{VO(H_2PO_4)_2\}_n$ exclusively. Redetermination of crystal structure of $\{VO(H_2PO_4)_2\}_n$ reveals a layered two-dimensional structure without any organic moieties between the layers. In recent attempts Hutchings et al. have obtained polycrystalline oxo-vanadium(IV) phosphate compound which they have formulated as $VO(H_2PO_4)_2$.[39a] In their process $VOPO_4$ or $V_2O_5$ and $H_3PO_4$ were used as precursors, while aldehyde or ketone or alcohol was used as reducing agent. In our process we obtained a well-shaped single crystalline product of $\{VO(H_2PO_4)_2\}_n$ at variance with the Hutchings et al. procedure where powder $VO(H_2PO_4)_2$ product was formed.[39] It is noteworthy that the X-ray powder diffraction patterns of the oxo-vanadium(IV) phosphate compound prepared by Hutchings et al. do not match with the XRD pattern of our compound. Nevertheless, the XRD powder pattern of $\{VO(H_2PO_4)_2\}_n$ calculated from single crystal X-ray data and the measured XRD pattern of $\{VO(H_2PO_4)_2\}_n$ were well-matched in our case (Figure 1). This clearly shows that the integrity of the bulk $\{VO(H_2PO_4)_2\}_n$ compound obtained in the hydrothermal process is excellent.

**Structure of $\{VO(H_2PO_4)_2\}_n$.** The equatorial O atoms of each $VO_5$ pyramid are shared with four $H_2PO_4$ tetrahedra in which the P atoms lie on the crystallographic 2-fold axes, and each $H_2PO_4$ tetrahedron in turn connects two adjacent distorted $VO_5$ pyramids to form a two-dimensional layer parallel to the *ab* plane (Figure 2) built with motifs of square $V_4P_4O_8$ having dimensions 6.39 Å × 6.39 Å (Figure 3). Two of the oxygen atoms (O2 and its symmetry related one) of the $H_2PO_4$ groups link the neighboring V atoms in the layer, while the remaining two oxygen atoms (O3 and its symmetry related one) of $H_2PO_4$
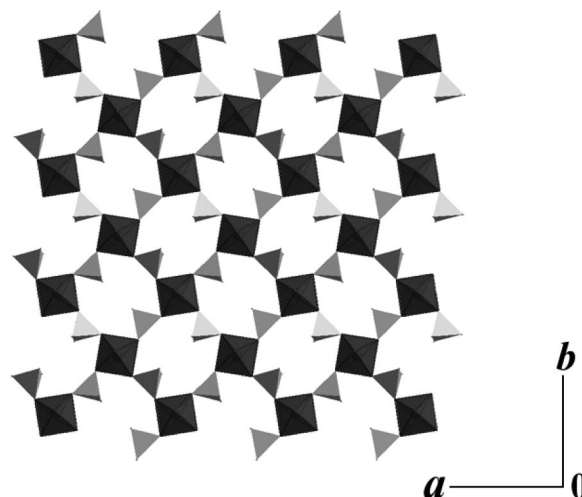


**Figure 2.** Drawing showing the interlinking of $VO_5$ square-pyramid and $H_2PO_4$ tetrahedra forming a (110) layer.
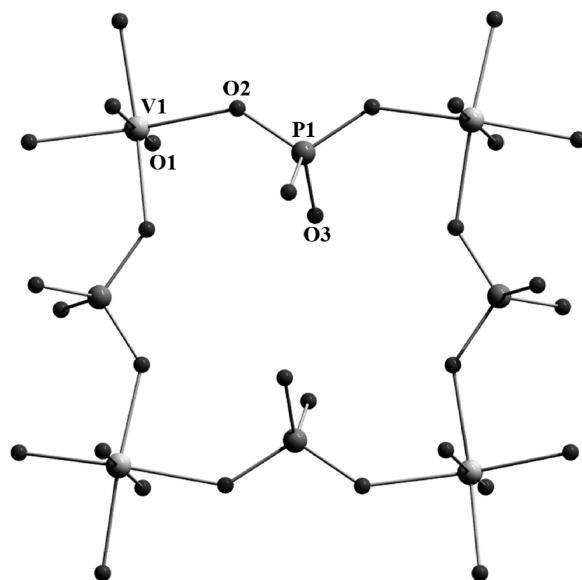


**Figure 3.** Diagram showing the formation of the $V_4P_4O_8$ square motif in $\{VO(H_2PO_4)_2\}_n$.

groups are terminal with relatively long P−O bond distances, P1−O3 1.571(3) Å, indicating P−OH groups. The bond valence sum ($S$) for V in $\{VO(H_2PO_4)_2\}_n$ was calculated according to eq 1:[42a]

$$S = \exp[(r_0 - r)/B] \tag{1}$$

where $r_0$ ($V^{4+}$−O) = 1.784 Å and $B$ is 0.37. The calculated value of $S$, 4.13, is in good agreement with the expected value of 4.0 for V(IV).[42] The two-dimensional parallel layers are separated by ca. 3.99 Å and are staked along the crystallographic [001] direction. Additional weak interaction exists between the vanadium center and vanadyl oxygen atom (O1) of the next molecule at $(^1/_4, ^1/_4, ^1/_2 + z)$ with a V1$\cdots$O1 distance of 2.412(6) Å. Inclusion of oxygen (O1) into bond valence sum calculation affords $S = 4.32$. However, this weak interaction between vanadium center and vanadyl oxygen interlinks the parallel layers of $VO_5$ polyhedra. Notably magnetic property of $\{VO(H_2PO_4)_2\}_n$

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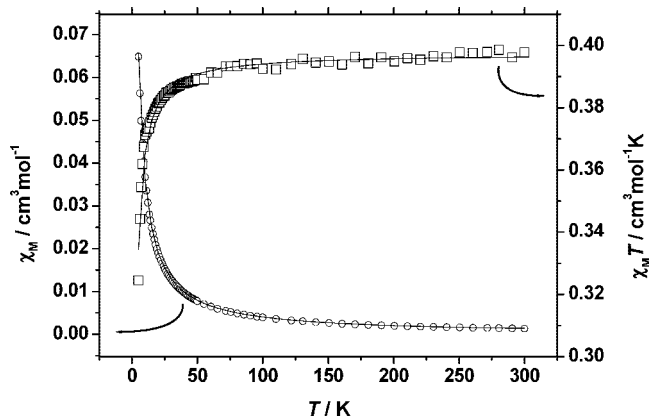
**Figure 4.** $\chi_M T$ product vs $T$ ($\square$) and $\chi_M$ vs $T$ ($\bigcirc$) plot for compound $\{VO(H_2PO_4)_2\}_n$. Solid lines represent the best fit of the data with the model described in the text. Arrows indicate the corresponding scales.

is explicable on the basis of its two-dimensional layered structure (see below). It seems, therefore, the distal interaction between vanadyl oxygen (O1) and the vanadium(IV) ion present in the next layer has no apparent influence on the magnetic property of the compound. The additional reinforcement between the layers is provided by intermolecular O−H···O interaction (O3···O3 2.826(4) Å, H(O3)···O3 2.27 Å, O3−H(O3)···O3 125°) in which the hydroxyl O3 atom in the molecule at $(x, y, z)$ acts as a donor to the O3 atom in the molecule at $(y - {}^1/_2, 1 - x, 1 - z)$.

**Magnetic Study.** The temperature dependence of the molar magnetic susceptibility, $\chi_M$, for $\{VO(H_2PO_4)_2\}_n$ was measured in the temperature range 2−300 K under a magnetic field of 1 T. The $\chi_M T$ value of 0.398 cm$^3$ mol$^{-1}$ K at 300 K for $\{VO(H_2PO_4)_2\}_n$ is slightly higher than the value expected for a magnetically isolated oxo-vanadium(IV) ion ($\chi_M T = 0.375$ cm$^3$ mol$^{-1}$ K for $g = 2.0$ and $S = {}^1/_2$) (Figure 4). Upon cooling, the $\chi_M T$ value for $\{VO(H_2PO_4)_2\}_n$ remains almost unaltered with temperature until ca. 40 K and then decreases abruptly reaching a minimum of 0.324 cm$^3$ mol$^{-1}$ K at 2 K, indicating an antiferromagnetic behavior. The antiferromagnetic nature of the interactions is confirmed by comparing the data sets with the Curie−Weiss expression. The fitting of the Curie−Weiss equation in the above-said temperature region yields $\theta = -1.96(1)$ K for $\{VO(H_2PO_4)_2\}_n$, indicating the presence of weak antiferromagnetic interaction.

In order to model the magnetic properties of $\{VO(H_2PO_4)_2\}_n$, we first attempt to fit the magnetic susceptibility data to the analytical expressions for dimeric and chain systems and introducing a mean field term $(zJ')$ to account for the interdimer or interchain interactions.[43] However, neither the dimer nor the chain model could satisfy the observed $\chi_M (T)$ data. X-ray structure analysis shows that the compound $\{VO(H_2PO_4)_2\}_n$ possesses a layered structure in which each $VO^{2+}$ moiety is connected to its four nearest neighbors by $H_2PO_4^-$ bridging ligands that afford the superexchange pathway. On the basis of the site symmetry of the vanadium atom, the extended structure of $\{VO(H_2PO_4)_2\}_n$ is likely to generate the square 2D magnetic layers. Two-dimensional layers of interconnected oxo-vanadium(IV) centers (d$^1$) with $S = {}^1/_2$ spin system is capable to give rise to a quantum Heisenberg antiferromagnet (QHAF).[19,21] The analytical expression for the magnetic susceptibility of such type of 2D QHAFs is available in the literature that allows determination of the $J$ and $g$ values from susceptibility data.[19] Accordingly, the observed

magnetic susceptibility data for $\{VO(H_2PO_4)_2\}_n$ were fitted to an expression as given below:[44]

$$\chi_M = \frac{C}{T} \frac{1 + \left\{ \sum_{n=1}^{5} a_n \left( \frac{-J}{T} \right)^n \right\}}{1 + \left\{ \sum_{n=1}^{5} b_n \left( \frac{-J}{T} \right)^n \right\}} \tag{2}$$

where $C = 0.375g^2$ and the coefficients $a_n$ and $b_n$ are given in ref 19. The best fit parameters were $J/k_B = -0.314(1)$ K and $g = 2.05(1)$ with an agreement factor $R = 4.7 \times 10^{-6}$.

The $\chi_M$ versus $T$ curve (Figure 4) does not go through a rounded maximum for compound $\{VO(H_2PO_4)_2\}_n$, a feature which is usually observed for a bulk antiferromagnetic system indicating that $\{VO(H_2PO_4)_2\}_n$ does not experience any long-range ordering down to 2 K. $T_{max}$, the temperature at which the $\chi_M$ value becomes maximum may be calculated for this type of antiferromagnetic system using the relation, $T_{max} = 0.936J/k_B$.[45] For $\{VO(H_2PO_4)_2\}_n$, $T_{max}$ thus calculated is 0.29 K. Hence, this temperature (0.29 K) is beyond the limit of our magnetometer for observing a knee-shaped $\chi_M$ versus $T$ plot for compound $\{VO(H_2PO_4)_2\}_n$.

Quite a few copper(II) salts and coordination complexes have been prepared and characterized structurally as well as magnetically with reference to their 2D QHAF properties,[14,15,18−20,46−51] but report of structural and magnetic characterization of vanadium(IV) layered compounds is very rare.[19,21] The intralayer antiferromagnetic interactions in $\{VO(H_2PO_4)_2\}_n$ is weak; however, such type of weak interactions were also observed in some copper-based QHAFs in earlier studies.[18] Nevertheless, the present study keeps promise for more intensive studies of this type of system to understand the underlying mechanism of intralayer antiferromagnetic interactions in vanadium-based QHAFs.

**Nitrogen Sorption Study.** The nitrogen sorption measurements of $\{VO(H_2PO_4)_2\}_n$ were undertaken to calculate the surface area of the catalyst. BET surface area ($S_{BET}$) of $\{VO(H_2PO_4)_2\}_n$ was calculated from the N$_2$ adsorption isotherms. The sorption experiments showed that the $\{VO(H_2PO_4)_2\}_n$ has the BET surface area of 2.01 m$^2$ g$^{-1}$. $S_{BET}$ of VO(H$_2$PO$_4$)$_2$ was found to be 1.62 m$^2$ g$^{-1}$ in an earlier study.[52]

**Epoxidation Reactions.** The catalytic properties of oxo-vanadium(IV) and oxo-vanadium(V) complexes are well established.[53] Oxo-vanadium(IV) complexes catalyze the epoxidation reaction of olefins in homogeneous and heterogeneous medium, and the mechanism involved in these reactions is also well established.[25−27] VO(H$_2$PO$_4$)$_2$ was reported to form as an impurity during the preparation of the VOHPO$_4$·0.5H$_2$O type

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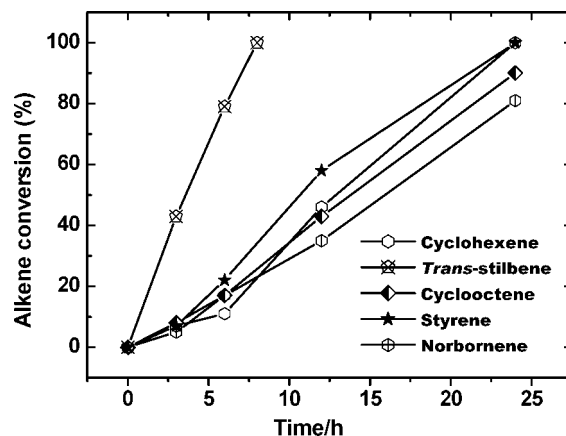
**Table 1. Epoxidation of Olefins with *tert*-BuOOH Catalyzed by $\{VO(H_2PO_4)_2\}_n^f$**

| substrate | reaction time (h) | conversion (wt%) | % yield of products | | TON[e] |
|---|---|---|---|---|---|
| | | | epoxide | others | |
| (cyclohexene) | 24 | 100 | 82 | 18[a] | 1582 |
| (cyclooctene) | 24 | 90 | 80 | 10[b] | 1064 |
| (norbornene) | 24 | 81 | 100[c] | -- | 1120 |
| (styrene) | 24 | 100 | 44 | 66[d] | 1249 |
| (trans-stilbene) | 8 | 100 | 100 | -- | 722 |

[a] 2-Cyclohexen-1-ol. [b] Cyclooctene-1-ol and cyclooctene-1-one were formed. [c] *exo*-epoxynorbornane. [d] Benzaldehyde and benzoic acid were formed. [e] Turnover number (TON) = moles converted/mol of active site. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified by Varian CP-3800 gas chromatograph equipped with an FID detector and a CP-Sil 8 CB capillary column. [f] Reaction conditions: alkenes (1 g); catalyst (2 mg); TBHP (2 mL); acetonitrile (8 mL). Temperature 70 °C.

catalyst and implicated for poor activity of these materials.[54] Later it was observed that $VO(H_2PO_4)_2$ is highly selective in catalytic oxidation of butane and butene.[39a] However, oxo-vanadium(IV) phosphate catalyzed epoxidation reactions have never been explored. In this study $\{VO(H_2PO_4)_2\}_n$ is found to be highly efficient in catalyzing epoxidation reactions of olefins with *tert*-BuOOH in heterogeneous condition. Epoxides are very useful and versatile intermediates for the synthesis of many commodity and fine chemicals as well as pharmaceuticals and agrochemicals. Alkyl-hydroperoxides are used on a large scale in industrial epoxidation, for example, in Halcon-Arco and Sumitomo processes.[55,56] The recycling of coproducts, e.g., *tert*-BuOH has been realized in the Sumitomo process. Aromatic and aliphatic alkenes react with *tert*-BuOOH to produce epoxides with remarkable selectivity in good yield using $\{VO(H_2PO_4)_2\}_n$ as heterogeneous catalyst in acetonitrile. The results of the catalytic epoxidation of different substrates are given in Table 1. The oxidation of cyclohexene (Figure 5) goes smoothly, showing an excellent conversion (100%) to form cyclohexene oxide as the major product with 82% selectivity; along with this, 2-cyclohexen-1-ol was also produced owing to allylic C−H oxidation. Epoxidation of cyclohexene with *tert*-BuOOH has been studied using $VO(acac)_2$ (acac = acetylacetonate) as catalyst under homogeneous and heterogeneous condition. Interestingly efficacy of catalyst has been enhanced upon heterogenization of $VO(acac)_2$ onto polymer matrix.[57] In homogeneous condition $VO(acac)_2$ catalyst yields 10−12% of cyclohexene oxide while vanadyl ion, anchored to a polystyrene support through acetyl-lacetonate ligands, gave yields of cyclohexene oxide up to 26%, more than a 2-fold increase over the homogeneous condition.[57] Bulkier cycloalkenes such as norbornene and cyclooctene (Table 1) have also been successfully converted to selectively *exo*-



**Figure 5.** Reaction profile for the epoxidation of olefins with *tert*-BuOOH catalyzed by $\{VO(H_2PO_4)_2\}_n$.

epoxynorbornane (conversion ∼81%, selectivity 100%) and cyclooctene oxide (conversion ∼90%, selectivity 80%), respectively. Oxidation of styrene showed a 100% conversion, but the epoxide yield was 44% while the combined yield of benzaldehyde and benzoic acid was 56%. This showed that in the reaction conditions styrene−epoxide undergoes further oxidation producing benzaldehyde and benzoic acid. However, in the case of *trans*-stilbene, the epoxidation reaction showed remarkable epoxide selectivity yielding 100% epoxide in 8 h. The overall catalytic efficacy of $\{VO(H_2PO_4)_2\}_n$ in epoxidation reactions was remarkable, which is reflected in the high turnover numbers for all the olefinic substrates (Table 1). Epoxidation of cyclohexene, *trans*-stilbene and styrene with *tert*-BuOOH over a variety of vanadium containing catalysts under heterogeneous conditions has been studied in the recent past (Table 2). Venkatathri et al. studied epoxidation of cyclohexene over different vanadium−aluminum−phosphate (VAPO) catalysts which showed up to 85% epoxide selectivity, however, with low turnovers.[58] Selectivity of the *trans*-stilbene epoxide improves (100%) on immobilization of the VO(Saloph) complex (Saloph = $N,N'$-*o*-phenylene-bis-(salicylidenaminato)) into Y zeolite or mesoporous silica matrix while the yield remains within 42%. Notably, a 93% yield of *trans*-stilbene epoxide is obtained only upon addition of a 14-fold excess of *tert*-BuOOH using different Mn-containing molecular sieves in the earlier studies.[59] Particularly in this reaction the performance of $\{VO(H_2PO_4)_2\}_n$ was remarkable (Table 2). In the case of styrene epoxidation, the VO(Saloph) complex again exhibited improvement of the yield of epoxide on immobilization into zeolitic matrices; however, the yields were not impressive.[60] In fact, in the epoxidation of styrene with *tert*-BuOOH over transition metal immobilized zeolite or molecular sieve catalysts, epoxide selectivity seldom goes above 40% in the earlier studies.[4d,53a] In our recent attempt we have succeeded to improve the yield of styrene epoxide up to 86% using copper(II) Schiff-base anchored MCM-41 catalyst.[4d]

To test if vanadium is leaching from the solid catalyst during reaction, the liquid phase of the reaction mixture is collected by filtration at the reaction temperature after 30% of the epoxidation reaction is completed. Atomic absorption spectrometric analysis of the liquid phase of the reaction mixtures thus collected by filtration confirms that vanadium is absent in the liquid phase.

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**Table 2. Epoxidation of Alkenes with *tert*-BuOOH Catalyzed by a Variety of Vanadium-Based Catalysts**

| catalyst | conversion (wt %) | yield of epoxide (%) | TON[a] | ref |
|---|---|---|---|---|
| | | cyclohexene | | |
| VO(acac)$_2$ | 12 | 12 | | 57 (homogeneous medium) |
| polystyrene supported VO(acac)$_2$ | 26 | 26 | 34 | 57 |
| VAPO-31AQ | 100 | 70 | 44 | 58 |
| VAPO-31NA | 100 | 85 | 90 | 58 |
| VAPSO-Amr | 100 | 44 | 50 | 58 |
| {VO(H$_2$PO$_4$)$_2$}$_n$ | 100 | 82 | 1582 | this work |
| | | *trans*-stilbene | | |
| VO(Saloph) | 9 | 7 | 256 | 60 (homogeneous medium) |
| VO(Saloph)-Y | 37 | 31 | 1013 | 60 |
| VO(Saloph)-MCM-41 | 48 | 42 | 1324 | 60 |
| {VO(H$_2$PO$_4$)$_2$}$_n$ | 100 | 100 | 722 | this work |
| | | styrene | | |
| VO(Saloph) | 11 | 1 | 726 | 60 (homogeneous medium) |
| VO(Saloph)-Y | 35 | 12 | 2362 | 60 |
| VO(Saloph)-MCM-41 | 41 | 18 | 2753 | 60 |
| {VO(H$_2$PO$_4$)$_2$}$_n$ | 100 | 44 | 1249 | this work |

[a] TON = moles converted/moles of active site. Saloph = $N,N'$-$o$-phenylene-bis-(salicyliden-aminato).

It is noticed that after filtration of the {VO(H$_2$PO$_4$)$_2$}$_n$ catalyst from the batch reactor at the reaction temperature, epoxidation reactions do not proceed further. Vanadium is also not detected in the liquid phase of the reaction mixture after the completion of the reaction. These experiments clearly demonstrate that vanadium is not leaching out from the solid catalyst during epoxidation reactions. To test if oxygen in air has any influence on the catalytic epoxidation of olefins, the reactions were performed in an Ar atmosphere. Dissolved oxygen present in the reaction mixture was first removed by bubbling pure N$_2$ gas into it. The whole setup was then evacuated and argon gas is introduced into the batch reactor. Prior to addition of *tert*-BuOOH, the evacuation and introduction of argon are repeated for three times, and finally dry argon is introduced into the reactor. The epoxidation reactions have been followed as described above. The percentage of conversion obtained for different olefins in epoxidation reaction under Ar atmosphere has been collated in ref 61. Comparison of the percentage of conversion of olefins in air and in Ar convincingly demonstrates that oxygen present in the air has no influence in the catalytic reactions (Table 1 and ref 61). The small difference (1−2%) in the percentage of conversion, in two different reaction atmospheres, can be attributable due to the error involved in GC analysis.

The structural integrity of the recovered catalyst has been verified by X-ray powder diffraction measurements. After the catalytic reactions are over, solid catalyst was recovered by centrifugation and washed with fresh acetonitrile several times and dried in air oven. The recovered catalyst was then subjected for X-ray powder diffraction analysis. Comparison of X-ray diffraction patterns of the recovered catalyst and pristine {VO(H$_2$PO$_4$)$_2$}$_n$ indicates that the overall structure of the catalyst is remained unaltered after the epoxidation reactions. No change in color of the solid catalyst was observed upon addition of hydroperoxide. Notably the recovered catalyst can be reused in catalytic reactions for several times with no considerable loss of activity (first run, cyclohexene conversion = 100%; second run, cyclohexene conversion = 97%; third run, cyclohexene conversion = 100%. No induction period was observed in all the reactions (Figure 5).

## Concluding Remarks

In summary, we have succeeded in preparing a novel compound {VO(H$_2$PO$_4$)$_2$}$_n$ by following a routine hydrothermal process. This compound demonstrates interesting catalytic and magnetic properties. {VO(H$_2$PO$_4$)$_2$}$_n$ has shown excellent catalytic activities in epoxidation reactions toward various industrially important olefinic substrates. The layered structure of {VO(H$_2$PO$_4$)$_2$}$_n$ seems to facilitate the easy access of the oxidant and reactants into the interior of the solid catalyst. It is noteworthy that epoxidation of *trans*-stilbene with *tert*-BuOOH catalyzed by {VO(H$_2$PO$_4$)$_2$}$_n$ displays a remarkable yield of the corresponding epoxide. Such a high yield has rarely been achieved in the earlier studies.[53a,59,60] The magnetic property of this compound has been explained in terms of quantum Heisenberg antiferromagnet model. Examples of V(IV) based QHAF systems are rare in the literature. Certainly hydrothermal synthesis of {VO(H$_2$PO$_4$)$_2$}$_n$ together with its magnetic study demonstrate an avenue to design new type of vanadium-based QHAF systems that have potential to afford in-depth understanding of the exotic phenomenon of low-dimensional magnetism.

**Supporting Information Available:** Further details of structure determination including tables of crystal data, atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, an ORTEP diagram showing atom numbering scheme for the {VO(H$_2$PO$_4$)$_2$}$_n$, a polyhedral view down the crystallographic *c*-axis showing the stacking of 2D layers of {VO(H$_2$PO$_4$)$_2$}$_n$, and N$_2$ adsorption isotherms of the catalyst measured at 77 K. This information is available free of charge via the Internet at http://pubs.acs.org.

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(61) Percentage of conversion (wt %) in olefin epoxidation reactions (in Ar atmosphere) for different substrates were as follows: cyclohexene, 100%; cyclooctene, 92%; norbornene, 82%; styrene, 98% and *trans*-stilbene, 99%.