Polyhedron 69 (2014) 1-9

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Heterogeneous catalytic oxidation of styrene by an oxo bridged divanadium(V) complex of an acetohydrazide-Schiff base



POLYHEDRON

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ARTICLE INFO

Article history: Received 20 June 2013 Accepted 6 November 2013 Available online 15 November 2013

Keywords: μ-Oxido divanadium compound Crystal structure Catalytic oxidation of styrene Al₂O₃ support Catalyst recycling

ABSTRACT

We have synthesized a μ -oxido divanadium compound [(VOL)₂(μ -O)] with an aliphatic hydrazone ligand LH₂ = (E)-N'-(1-(2-hydroxyphenyl)ethylidene)acetohydrazide. The complex was characterized by elemental analysis, IR and UV–Vis spectroscopy and the molecular structure was established by single crystal X-ray diffraction technique. The complex has been infused over alumina to prepare a heterogeneous catalyst which was characterized by IR spectroscopy, thermogravimetric and powder XRD analyses. The catalyst has been studied for the oxidation of styrene in presence of H₂O₂ and appears to be easily recyclable. A conversion of 99.7% and selectivity of 88.1% for benzaldehyde formation and a turnover number of 1354 was detected under the most favorable reaction conditions.

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1. Introduction

Vanadium is a versatile bio-essential element. Its presence in vanadate-dependent haloperoxidases [1,2] and vanadium-nitrogenases [3], its therapeutic application as insulin-enhancing agent in treatment of diabetes [4–10] and anticancer activity [11–14] have stimulated a considerable amount of research. Possible pharmacological activities of vanadate compounds are supported by the coordinating ligands. Chelation improves absorption, transportability and uptake of the metal ions into cells, thus reducing the necessary dose of efficacy as well as the metal ion toxicity [15]. Vanadium ion in coordination complexes is capable of existing in a range of oxidation states from 3+ to 5+ and possesses unusual redox ability. In 4+ and 5+ oxidation states, vanadium is highly redox active and acts as strong Lewis acid due to low radius to charge ratio, which can stimulate various organic transformation reactions [16]. The role of vanadium-based compounds as efficient catalysts attests the applicability of this metal ion in bulk industrial productions, viz., the use of oxovanadium complexes in asymmetric synthesis [17-21], in C-C bond formation as well as C-C, C-O and C-H bond cleavages [22-26], involvement as an intermediate in hydrosulfurization of crude oils [27], oxidative halogenation and selective epoxidation of unsaturated hydrocarbons and allyl alcohols [22,28].

Acid hydrazides R–CO–NH–NH₂ and their corresponding hydrazones with aromatic carbonyl compounds R-CO-NH-N = CR¹R² are the N/O donor ligands that can act as neutral as well as anionic chelator towards metal ions and have remarkable biological importance [29]. Additionally, hydrazone metal complexes have also attracted research interest for their possible pharmacological applications [30] antimicrobial, antitumor activities [31] and also in catalysis [32]. The usefulness of both vanadium and hydrazone Schiff bases prompted us to investigate the structure-activity studies of vanadium-hydrazone chelate complexes. There are few reports on the structures and solution state properties of vanadium complexes of hydrazone Schiff bases derived by the condensation of an aroyl hydrazide with an aromatic carbonyl compound [33]. A very few have been investigated for their catalytic potential [34]. In this paper we are concerned about the structural investigation and catalytic activity of a vanadium complex chelated by a hydrazone ligand, which is the condensation product of a less investigated alkyl hydrazide with an aromatic ketone.

In search of catalysts for organic transformations we have directed our research on immobilization of complexes on various solid supports. As benefits of this process, in many cases these catalysts (or catalyst precursors) are easily recyclable and maintain their activity after several catalytic cycles. Although the solid support can constitute a protective environment around the metal complex, the physical restrictions imposed by the matrix can make the access of reactants to the metal centre more difficult compared to homogeneous system affecting the conversion and sometimes selectivity [35].

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^{0277-5387/\$ -} see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2013.11.007

Catalytic oxidation of styrene using H_2O_2 may give rise to several products. Formation of at least five products such as styrene oxide, benzaldehyde, benzoic acid, phenylacetaldehyde and 1-phenylethane-1,2-diol has been reported [36]. Benzaldehyde is obtained with the highest yield due to fast conversion *via* nucleophilic attack of H_2O_2 on styrene oxide followed by the cleavage of hydroperoxystyrene intermediate.

A recent review by Chaudhury et al. [37] admits the existence of at least thirty structurally characterized µ-oxido divanadium compounds containing a $[V_2O_3]^{n+}$ (*n* = 4, 3 and 2) core where both metal centers are chelated by identical ligand molecules [33a,38-42]. The V-O-V bridging angle and the orientation of the terminal V=O groups with respect to each other as well as to the bridging oxo ligand are characteristic features of these species. With octahedral vanadium centers most of these complexes have a linear V-O-V bridge with the terminal V=O groups mutually trans located (*anti*-linear structure) [38]. On the other hand, when the vanadium centers have square pyramidal geometry [33a,39–42], the terminal and bridging oxo atoms have diverse range of arrangements (Scheme 1), hovering between anti-linear (i) [41] and syn-angular (iv) [39] through anti-angular (ii) [33a,40] and twist angular (iii) [42] conformations. In the present case the $[V_2O_3]^{4+}$ core structure is guite unconventional. Both the vanadium centers are squarepyramidal with the terminal V=O groups *cis* to the bridging oxo ligand but acquire anti-angular orientation with respect to eachother.

Here we report the synthesis and characterization of a μ -oxido divanadium compound [(VOL)₂(μ -O)] with the aliphatic hydrazone ligand LH₂ = (E)-N'-(1-(2-hydroxyphenyl)ethylidene)acetohydrazide, along with its catalytic activity for oxidation of styrene using H₂O₂ as oxidant under heterogeneous condition. The synthesized complex was heterogenized by supporting onto anhydrous alumina (Al₂O₃). The catalyst, [(VOL)₂(μ -O)]/Al₂O₃ was characterized by thermogravimetric analysis, IR spectroscopy, powder X-ray diffraction and BET surface area analysis. Catalytic activity for the oxidation of styrene was evaluated by varying different parameters such as reaction temperature, time, molar ratio of styrene to H₂O₂ and amount of the catalyst. The recycled catalyst has also been thoroughly characterized and its activity was evaluated under optimized conditions.

2. Experimental

2.1. Materials

All solvents were of reagent grade and used without further purification. Acetic hydrazide and 2-hydroxyacetophenone were



Scheme 1. Possible conformations of the $[V_2O_3]^{n+}$ (n = 4, 3, and 2) cores with respect to bridging and terminal oxygen atoms in μ -oxido divanadium complexes, (i) *anti*-linear, (ii) *anti*-angular, (iii) twist-angular, (iv) *syn*-angular and (v) an unconventional *anti*-angular conformation with *syn* orientation of the bridging oxygen with respect to both terminal oxygens in the present $[(VOL)_2(\mu-O)]$ complex.

purchased from Aldrich Chemical Company and used as received. VO(acac)₂ was prepared by the procedure described below. In a solution containing sodium carbonate (5.0 g) and acetylacetone (5 mL) in distilled water was added a second solution of VO(SO₄) - × H₂O (5 g) in 15 mL distilled water. The mixture was warmed in a steam bath for precipitation of VO(acac)₂ and then allowed to cool in ice. The solid was then filtered, washed with ice cold water, dried on a steam bath and kept in CaCl₂ desiccator for further use. Neutral active Al₂O₃ (Activity I-II, according to Brockmann, Loba chemie, Mumbai) was used as received. Dichloromethane, 30% aqueous H₂O₂ and styrene were obtained from Merck and used as received.

2.2. Physical measurements

C, H and N microanalyses were carried out with a Perkin-Elmer 2400 II elemental analyzer. The Fourier Transform Infrared spectra were recorded in the range 4000–400 cm⁻¹ on a Perkin-Elmer RX I FT-IR spectrophotometer with solid KBr pellets. The electronic spectra in HPLC grade acetonitrile were recorded at 300 K on a Perkin-Elmer Lambda 40 (UV-Vis) spectrometer in a 1 cm quartz cuvette in the range 800–200 nm. Thermogravimetric analyses of the complex and the catalyst was carried out on a SII EXSTAR6000 TG/DTA 6300. The experiments were performed in N₂ at a heating rate of 10 °C min⁻¹ in the temperature range 25–500 °C using an alumina pan. The powder X-ray diffraction (XRD) patterns of the samples were recorded with a Scintag XDS-2000 diffractometer using Cu K α radiation. Adsorption–desorption isotherms of samples were recorded on a micromeritics ASAP 2010 surface area analyzer at –196 °C.

2.3. Syntheses

2.3.1. Synthesis of the hydrazone ligand [LH₂]

LH₂ [(E)-N'-(1-(2-hydroxyphenyl)ethylidene)acetohydrazide] was prepared by the condensation of acetic hydrazide (0.74 g, 10 mmol) in 200 mL of methanol with 2-hydroxyacetophenone (1.362 g, 10 mmol) in presence of a single drop of glacial acetic acid (catalyst). On refluxing the methanolic solution for 5 h a colorless solution was obtained. The solvent was removed under reduced pressure and the white residue was purified by crystallization from MeOH. Colorless shiny crystals were obtained. Yield 0.177 g (92%). *Anal.* Calc. for C₁₀H₁₂N₂O₂ (*M* = 192.1 g/mol): C, 62.49; H, 6.29; N, 14.57. Found: C, 62.58; H, 6.23; N, 14.49%. FT-IR bands (KBr, cm⁻¹): v(C=N) 1606, v(C=O) 1667.

2.3.2. Synthesis of the complex $[(VOL)_2(\mu-O)]$

The complex was synthesized by adding solid VO(acac)₂ (0.270 g, 1 mmol) to 30 mL acetonitrile solution of LH₂ (0.192 g, 1 mmol). The mixture was stirred for half an hour at 60 °C. The dark brown solution was then cooled to room temperature, filtered and kept for slow evaporation of solvent. Dark brown square crystals appeared on standing overnight. Yield 0.296 g (56%). *Anal.* Calc. for C₂₀H₂₀N₄O₇V₂ (*M* = 530.28 g/mol): C, 45.30; H, 3.80; N, 10.56. Found: C, 45.38; H, 3.75; N, 10.60%. FT-IR bands (KBr, cm⁻¹): $v_{C=N}$ 1542, v_{C-O} (phenolate) 1383, v_{C-O} (enolate) 1301, v_{N-N} 1082, $v_{V=O}$ 988 and $v_{V-(\mu-O)-V}$ 875. UV–Vis bands (acetonitrile, nm): $\pi \to \pi^*$ 272, LMCT 370.

2.3.3. Synthesis of the catalyst

The catalyst containing 15% of the complex $[(VOL)_2(\mu-O)]$ was synthesized by impregnating 1 g of Al_2O_3 with a solution of $[(VOL)_2(\mu-O)]$ (0.15 g in 15 ml of acetonitrile) with stirring for 35 h and dried at 100 °C for 10 h. The obtained material was designated as $[(VOL)_2(\mu-O)]/Al_2O_3$.

2.4. Crystallographic data collection and structure refinements

Intensity data were collected on a Cu rotating anode equipped with a Brucker CCD2000 detector ($\lambda = 1.54178$ Å) 293 K. Data collection was performed with the 'Nonius, Supergui' program [43]. Programs Denzo and Scalepack [44] were used for data reduction. The structure was solved by direct methods [45] and refined by full-matrix least-squares method with program SHELXL-97 [46]. All non hydrogen atoms were refined anisotropically by full-matrix least-squares based on F^2 . The H atoms were generated geometrically and included in the final cycles of refinement in the riding model approximation. Selected crystallographic data, experimental conditions and relevant features of the structural refinement for the complex are summarized in Table 1.

2.5. Catalytic reaction procedure

The oxidation reaction was carried out in a borosilicate glass reactor provided with a double walled condenser. The desired catalyst, styrene and H_2O_2 mixtures were intensively stirred in the reactor at the set constant temperature for the whole duration of the reaction. The same reaction was carried out by varying the parameters such as the molar ratio of substrate to H_2O_2 , amount of the catalyst, reaction time and reaction temperature. After completion of the reaction, catalyst was removed and the product was extracted with dichloromethane. The product was dried with magnesium sulfate and analyzed on Gas Chromatograph using BP-1 capillary column. Product was identified by comparison with the authentic samples and finally by Gas Chromatography–Mass Spectroscopy (GC–MS).

3. Results and discussion

3.1. Crystal structure description

The ORTEP diagram of the complex is depicted in Fig. 1 and the bond lengths and angles are listed in Table 2. The complex is a μ -oxido divanadium compound containing a $[V_2O_3]^{4+}$ core. Two non equivalent $[LV = O]^+$ moieties centered at V1 and V2 are connected by an oxo bridge group (O2). Both halves of the molecule have

Table 1

Crystal data and details of crystal structure refinement.

Empirical formula	$C_{20}H_{20}N_4O_7V_2$
Formula weight	530.28
T (K)	293
λ (Å)	1.54180
Crystal system	triclinic
Space group	<i>P</i> 1̄ (No. 2)
a (Å)	8.2470(12)
b (Å)	8.4830(11)
c (Å)	17.7830(17)
α (°)	94.35(2)
β (°)	97.49(2)
γ (°)	116.70(2)
$V(Å^3)$	1089.2(3)
Ζ	2
D_{calc} (Mg/m ³)	1.617
μ (mm ⁻¹)	7.644
F(000)	540
Crystal size (mm ³)	$0.21\times0.15\times0.11$
θ range (°)	2.5-54.1
Reflections collected	19414
Independent reflections (R_{int})	2592 (0.085)
Data/parameters	2592/302
S	0.99
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0562, wR_2 = 0.1535$
$\Delta \rho (e \text{ Å}^{-3})$	0.43, -0.44
• • •	

square pyramidal geometry at the vanadium centers ($\tau = 0.095$ for V1 and 0.093 for V2) [47]. The ONO donor ligand LH₂ undergoes enolization at the amido (HN—C=O) fragment followed by double deprotonation to chelate three of the equatorial positions *via* the amido oxygen, imino nitrogen and the phenoxo oxygen atoms (O3, N1, O4 to V1 and O6, N3, O7 to V2). The fourth equatorial position of both metal centers is occupied by the bridging oxygen atom O2. A terminal oxygen takes up the apical position (O1 to V1 and O5 to V2). V1 and V2 atoms are displaced towards the terminal oxygen atoms by 0.464 and 0.449 Å, respectively, from their mean equatorial planes (O3/N1/O4/O2 plane for V1 and O6/N3/O7/O2 for V2). The trichelating ligand mean planes show large distortions from planarity (max displacements for C4 +0.224(8), O3 –0.304(6) Å in the first plane, C14 –0.409(7), O6 0.374(6) Å for the second) and they form a dihedral angle of 56.2°.

Of particular interest in the structure is the conformation of the $[V_2O_3]^{4+}$ core, which is a function of the steric requirement of the ligand and the coordination geometry of the metal center [37]. The V1-O2-V2 bridge angle is 110.7(3)°, second to the lowest reported value (109.3(6)°) of that angle in a single oxido bridged divanadium compound [48]. The terminal V=O groups have a rare anti-angular conformation with respect to each-other (Scheme 1) although both are syn to the bridging oxygen atom. The torsion angle between the two V= O_t bonds is 99.61° which indicates that the terminal V=O groups are almost orthogonally twisted. The V1...V2 distance is 2.957 Å, slightly shorter than beforehand reported µoxido $[V_2O_3]^{4+}$ complexes synthesized with hydrazone ligands [33a,45]. The V=O bond distances [1.571(6) and 1.567(6)Å], the vanadium to bridging oxygen bond distances [1.789(5) and 1.806(6) Å] and V-N ones [2.117(7) and 2.082(8) Å] are within the range of analogous oxovanadium-hydrazone complexes [33a].

3.2. Characterization of the complex [(VOL)₂(μ -O)] and the catalyst [(VOL)₂(μ -O)]/Al₂O₃

The synthesized complex and the catalyst were characterized by FT-IR, TGA and BET surface area. The FT-IR spectra of the complex and of the catalyst are presented in Fig. 2. The spectrum of the complex (Fig. 2a) exhibits imine stretching ($v_{C}=_{N}$) band at 1542 cm⁻¹ indicating the coordination of the imine nitrogen atom to the metal center [32]. The absorption at 1383 and 1301 cm^{-1} are due to the stretching of v_{C-Q} (phenolate) and v_{C-Q} (enolate) groups, respectively N-N stretching band of the azo-fragment emerged at 1082 cm⁻¹. A strong band appearing at 988 cm⁻¹ is the signature of terminal V=O stretching, whereas a moderately strong V-(μ -O)-V antisymmetric stretching was observed at 875 cm⁻¹ [37]. FT-IR spectrum of the catalyst (Fig. 2b) shows bands at 1600, 1395 and 1304 cm⁻¹ corresponding to $v_{C=N}$, v_{C-O} (phenolate) and v_{C-O} (enolate) respectively, indicating the presence of the complex over the surface of catalyst. Terminal V=O stretching and V-(μ -O)-V antisymmetric stretching bands are averaged in the catalyst, may be due to overlapping of bands of the complex with those of Al₂O_{3.} The shifting in the band values may be due to interaction of the complex with oxygen atoms of the Al₂O₃ surface.

TGA of the complex (Fig. 3a) shows mass loss of 3.36% within the range of 150–290 °C, corresponding to the loss of one oxygen atom (calculated value 3.02%), which implies cleavage of the V– (μ -O)–V bond and dissociation of the molecule in two monomeric units. The decomposition of the complex was observed in several steps from 250 °C. The data indicate that the complex is stable up to 250 °C. The TGA of the catalyst (Fig. 3b) shows initial mass loss 2.1% up to 150 °C likely due to the removal of adsorbed water molecules. No significant loss occurs up to 450 °C, indicating that the stability of the complex increases after supporting on Al₂O₃.



Fig. 1. ORTEP drawing of the complex (ellipsoids at 40% probability level).

 Table 2

 Bond lengths (Å) and angles (°) of the complex.

Bond lengths			
V1-01	1.571(6)	V2-02	1.806(6)
V1-02	1.789(5)	V2-05	1.567(6)
V1-03	1.938(7)	V2-06	1.946(6)
V1-04	1.804(6)	V2-07	1.810(6)
V1-N1	2.117(7)	V2-N3	2.082(8)
Bond angles			
01-V1-02	108.0(3)	02-V2-05	106.7(3)
01-V1-03	105.0(3)	02-V2-06	85.6(3)
01-V1-04	104.8(3)	02-V2-07	103.9(3)
01-V1-N1	97.7(3)	02-V2-N3	151.1(3)
02-V1-03	85.1(3)	05-V2-06	104.6(3)
02-V1-04	102.8(3)	05-V2-07	104.2(3)
02-V1-N1	150.6(3)	05-V2-N3	98.3(3)
03-V1-04	144.9(3)	06-V2-07	145.5(3)
03-V1-N1	74.3(3)	06-V2-N3	74.1(3)
04-V1-N1	83.8(3)	07-V2-N3	83.3(3)
		V1-02-V2	110.7(3)



Fig. 2. FT-IR spectra of (a) $[(VOL)_2(\mu-O)]$ and (b) $[(VOL)_2(\mu-O)]/Al_2O_3$.

The surface area of the catalyst $(93.19 \text{ m}^2/\text{g})$ expands significantly when the complex $(3.23 \text{ m}^2/\text{g})$ is supported over Al_2O_3 $(81 \text{ m}^2/\text{g})$.

3.3. Oxidation of styrene using hydrogen peroxide and the catalyst

Generally, styrene oxidation gives styrene oxide, benzaldehyde and benzoic acid in perceptible yield. However under the present reaction conditions, the major oxidation product obtained was benzaldehyde possibly because of the fast conversion of styrene oxide to benzaldehyde.

3.4. Effect of temperature

The effect of temperature on the oxidation of styrene was investigated at three different temperatures viz. 60, 80 and 100 °C, keeping the other parameters fixed: namely styrene amount (10 mmol), 30% H_2O_2 (30 mmol), catalyst (30 mg) and reaction time (24 h). The results shown in Fig. 4 reveal that 16.9%, 99.7% and 99.6% of conversion was found corresponding to the temperature of 60, 80 and 100 °C, respectively. At 80 °C, the conversion of styrene was 99.7% with 88% selectivity of benzaldehyde and 12% selectivity of benzoic acid. On the other hand at elevated temperature (100 °C), 99.6% styrene conversion was found with 79% selectivity of benzaldehyde and 21% selectivity of benzoic acid, i.e. a decrease in selectivity for benzaldehyde was observed. This is due to over oxidation of benzaldehyde to benzoic acid at elevated temperature. Hence, further optimization of the conditions was carried out at 80 °C temperature.

3.5. Effect of the amount of H_2O_2

In order to determine the effect of H_2O_2 on the oxidation of styrene to benzaldehyde, we studied four different styrene to H_2O_2 molar ratios (1:1, 1:2, 1:3, and 2:1), keeping other parameters fixed: namely catalyst (30 mg), temperature (80 °C) and reaction time (24 h). The results are shown in Fig. 5. Styrene to H_2O_2 molar ratio of 1:1 and 1:2 resulted in 27.3 and 68.8% conversion, respectively, and with styrene to H_2O_2 molar ratio of 1:3, conversion increased to be nearly 99.7%, keeping fixed all other conditions. However, conversion was found to remain almost the same (99%) when the styrene to H_2O_2 molar ratio was further changed to 1:4. Therefore, 1:3 M ratio of styrene to H_2O_2 was found to be the most favorable in terms of conversion of styrene.

3.6. Effect of the amount of catalyst

The amount of catalyst has a significant effect on the oxidation of styrene. Six different amounts of catalyst viz., 10, 15, 20, 25, 30 and 35 mg which contain a vanadium concentration (mole $\times 10^{-5}$) of 0.50, 0.75, 1.01, 1.26, 1.51, 1.76 were used, keeping fixed all other reaction parameters, namely temperature (80 °C), styrene amount (10 mmol), 30% H₂O₂ (30 mmol) and reaction time (24 h). The results are shown in Fig. 6, indicating 76.1%, 80.0%, 89.1%, 93.4%, 99.7% and 99.8% conversion corresponding to an amount of 10, 15, 20, 25, 30 and 35 mg of catalyst, respectively. Lower conversion of styrene into benzaldehyde at low quantity



Fig. 3. Thermogram of (a) [(VOL)₂(μ -O)] and (b) [(VOL)₂(μ -O)]/Al₂O₃.



Fig. 4. Effect of temperature;% Conversion is based on styrene; time = 24 h; molar ratio of styrene to H_2O_2 : 1:3; amount of catalyst = 30 mg.

of catalyst may be due to fewer catalytic sites. The maximum percentage conversion was observed with 30 mg catalyst, and this amount was taken as optimal.

3.7. Effect of time

The time dependence of catalytic solvent free oxidation of styrene was studied by performing the reaction of styrene (10 mmol) with 30% H_2O_2 (30 mmol) in presence of 30 mg of catalyst at 80 °C with constant stirring. The percentage of conversion was monitored at different reaction times. Fig. 7 shows that increasing the reaction time, the % conversion also increases. Initial conversion of styrene increased with the reaction time that more time is required for the formation of reactive intermediate (substrate + catalyst), which finally converted into the products. In addition Fig. 7 shows that maximum percentage conversion was observed for 24 h of reaction time.

Thus the best conditions for maximum % conversion of styrene to benzaldehyde are characterized by the mole ratio of styrene to H_2O_2 of 1:3, 30 mg of catalyst and 24 h reaction time at 80 °C.

3.8. Control experiment

The control experiments with Al_2O_3 and the complex were also carried out under optimized conditions with styrene and H_2O_2 . It can be seen from Table 3 that Al_2O_3 is inactive towards the



Fig. 5. Effect of mole ratio;% Conversion is based on styrene; time = 24 h; temperature = 80 °C; amount of catalyst = 30 mg.

oxidation of styrene indicating that the catalytic activity occurs in presence of the complex only. The same reaction was carried out by taking the active amount of the complex. It was found that the active catalyst (complex) gives 97.1% conversion of styrene



Fig. 6. Effect of amount of catalyst;% Conversion is based on styrene; time = 24 h; temperature = 80 °C; molar ratio of styrene to H_2O_2 : 1:3.

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Fig. 7. Effect of reaction time;% Conversion is based on styrene; amount of catalyst = 30 mg; temperature = 80 °C; molar ratio of styrene to H_2O_2 : 1:3.

with 87.7% selectivity of benzaldehyde. Almost the obtained same activity (99.7% conversion of styrene with 88.1% selectivity of benzaldehyde) for supported catalyst indicates that the complex is the real active species. Thus, we succeeded in supporting the complex onto Al_2O_3 without any significant loss in activity, hence overcoming the traditional problems of homogeneous catalysis.

3.9. Heterogeneity test

Heterogeneity test was carried out for the oxidation of styrene as an example. For a rigorous proof of heterogeneity, a test was carried out by filtering catalyst from the reaction mixture at 80 °C after 6 h and the filtrate was allowed to react up to 8 h. This reaction mixture and the filtrate were analyzed by gas chromatography. No change in the % conversion as well as % selectivity was found indicating that the present catalyst falls into category C, i.e. active species does not leach and the observed catalysis is truly heterogeneous in nature. The results are presented in Table 4.

3.10. Recycling of the catalyst

Oxidation of styrene was carried out with the recycled catalyst, under the optimized conditions. The catalyst was removed from the reaction mixture after completion of the reaction by simple filtration, washed with dichloromethane and dried at 100 °C. The catalyst was recycled in order to test its activity as well as stability. The obtained results presented in Table 5 point out that there was no appreciable change in selectivity. However, a little decrease in conversion was observed showing that the catalysts are stable and can be regenerated for repeated use.

Table	3
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Control	evneriments	for t	the ov	idation	of styrene.

Catalyst	% Conversion	% Selectivity Benzaldehyde
Al ₂ O ₃ [(VOL) ₂ (μ-Ο)] [(VOL) ₂ (μ-Ο)]/Al ₂ O ₃	97.1 99.7	- 87.7 88.1

% Conversion is based on styrene; amount of catalyst = 26.1 mg (Al₂O₃), 3.9 mg ([(VOL)₂(μ -O)]), 30 mg ([(VOL)₂(μ -O)]/Al₂O₃); molar ratio of styrene to H₂O₂: 1:3, temperature 80 °C.

Die	4	

Heterogeneity	test.
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Catalyst	% Conversion	% Selectivity Benzaldehyde
[(VOL) ₂ (µ-O)]/Al ₂ O ₃ (6 h)	19.8	93.4
Filtrate (8 h)	19.9	93.2

% Conversion is based on styrene; amount of catalyst = 30 mg; molar ratio of styrene to H_2O_2 : 1:3, temperature 80 °C.

3.11. Characterization of the regenerated catalyst

The catalyst, $[(VOL)_2(\mu-O)]/Al_2O_3$ was regenerated in order to test its stability. The regenerated material $(R-[(VOL)_2(\mu-O)]/Al_2O_3)$ was characterized by FT-IR, and powder X-ray diffraction in order to confirm the retention of the catalyst structure, after completion of the reaction.

The FT-IR data for the fresh as well as the regenerated catalysts are represented in Fig. 8. The characteristic FT-IR bands (Fig. 8a) for the catalyst appeared at 1600, 1395 and 1304 cm⁻¹, and similar bands (Fig. 8b) were shown by the regenerated catalyst. No appreciable shift in the FT-IR band position of the regenerated catalyst compared to the fresh catalyst indicates the stability of supported catalyst. The XRD pattern of the powder sample (Fig. S1) of $[(VOL)_2(\mu-O)]$ is maintained in the catalyst $[(VOL)_2(\mu-O)]/Al_2O_3$. A decrease in intensity occurs with broadening of peaks upon infusion of the complex with Al_2O_3 but the crystalline nature retains. The XRD pattern of the powdered sample of the fresh and regenerated catalyst (Fig. 9) replicate each other suggesting that no structural change occurs after completion of the catalyst.

3.12. Discussion

Oxidation of styrene to benzaldehyde occurs *via* the formation of styrene oxide intermediate [36]. H_2O_2 being a strong oxidant leads to the oxidative cleavage of the epoxide ring forming benzal-

Table 5			
Recycling	of	the	catalyst.

Catalyst	Cycle	% Conversion	% Selectivity	TON
			Benzaldehyde	
$[(VOL)_2(\mu-O)]/Al_2O_3$	Fresh	99.7	88.1	1354
	1	99.8	88.2	1345
	2	99.2	88.1	1347

% Conversion is based on styrene; amount of catalyst = 30 mg; molar ratio of styrene to H_2O_2 : 1:3, time 24 h; temperature 80 °C.



Fig. 8. FT-IR spectra of (a) [(VOL)₂(µ-O)]/ Al₂O₃ and (b) R-[(VOL)₂(µ-O)]/Al₂O₃.

dehyde. d⁰ Metal complexes with strong Lewis acidic character (Mo^{VI}, V^V, Ti^{IV}) catalyze the epoxide formation step. The isolation and characterization of the actual epoxidizing species have not yet achieved. It has been generally accepted that a metal-hydroperoxide intermediate is formed. Mimoun and co-workers synthesized vanadium(V) alkylperoxidic complexes with several chelating ligands [49] and suggested that the metal-(alkyl/hydro) peroxide complexes are the most probable epoxidizing species. Based on their suggestion, we have proposed a plausible mechanism of styrene oxidation reaction with H₂O₂ catalyzed by the present complex [(VOL)₂(μ -O)] (Scheme 2).

Styrene is a good Lewis base and is attracted by vanadium(V) (strong Lewis acid) and binds to the metal center by displacement



Fig. 9. Powder XRD pattern of fresh catalyst (black) and regenerated catalyst (red). (Color online.)

of the weakly coordinated hydroperoxy oxygen or from the axial position trans to the vanadyl oxygen. This atom arrangement around the vanadium center leads to a nucleophilic attack of the peroxo oxygen to the coordinated electron deficient styrene followed by a migratory insertion of styrene between the vanadium–oxygen bond (σ – π rearrangement) forming a pseudocyclic dioxametallocyclopentane. A rapid decomposition of the pseudocyclic moiety occurs by a 1,3 dipolar cycloreversion process resulting in the formation of epoxide and the vanadium(V) hydroxyl complex. The epoxide (styrene oxide) is converted to benzaldehyde via the nucleophilic attack of H₂O₂ on styrene oxide followed by the cleavage of hydroperoxystyrene intermediate (Scheme 2). Fig. 9 suggests that the powder XRD pattern of the regenerated catalyst closely matches that of the fresh catalyst justifying the recoverv and recyclability of the catalyst. Unfortunately, any of the intermediate species proposed in Scheme 2 could not be isolated.

Our group has previously reported the oxidation of styrene by a mononuclear oxovanadium(IV) complex [50] which resulted in 99.1% selectivity for benzaldehyde with TON 1151. The present dinuclear oxovanadium(V) complex shows a small decrease in benzaldehyde selectivity (88.1%) but a considerable increase in TON (1354) compared to the mononuclear complex. The increase in TON can be justified with the fact that each molecule of the present complex has two metal centers accessible to a hydroperoxide anion. Hence there is a greater probability of the nucleophilic attack to take place in the present dinuclear complex compared to the previously reported mononuclear complex. This hypothesis can further be rationalized comparing the catalytic efficacy of the present complex with respect to a number of mononuclear oxovanadium complexes immobilized on polymer support, encapsulated in aluminosilicate zeolite-NaY and also immobilized on ordered mesoporous silica (MCM-41) reviewed by Mourya et al. [36]. Maximum selectivity of benzaldehyde 82.4% with 52% conversion and TON = 8 is observed with the compound $[V^{IV}O(hpbmz)_2]$. Highest TON = 2753 was obtained with $[V^{IV}O(saldien)_2]$ -MCM-41 but only with 41% conversion and 7.7% selectivity of benzaldehvde and



Scheme 2. Mechanistic approach of oxidation of styrene to benzaldehyde catalyzed by [(VOL)2(µ-O)].

the best conversion (97%) was observed with $[V^VO_2(sal-ambmz)]-Y$ with TON = 151 and benzaldehyde selectivity 54.9%. Considering all these three factors together, the present catalyst [(VOL)₂ $(\mu$ -O)]/Al₂O₃ results in 99.7% conversion with benzaldehyde selectivity 88.1% and TON = 1354, the best result observed among the reported catalysts supported over metal oxides.

4. Conclusion

We have reported in the present work an oxido bridged dinuclear vanadium(V) complex with an aliphatic hydrazone ligand synthesized by the condensation of acetic hydrazide and 2hydroxyacetophenone. The complex contains a $[V_2O_3]^{4+}$ core with an unconventional orientation of the oxo groups, the terminal V=O groups having a rare anti-angular conformation with respect to each-other but both are syn to the bridging oxygen atom. The dinuclear vanadium(V) complex is an efficient catalyst for the oxidation of styrene to benzaldehyde by H_2O_2 when supported over alumina, and it was found to be reusable. A plausible mechanism for the catalytic reaction has been proposed.

Acknowledgements

Financial assistance from CSIR [project no. 01(2491)/11/EMR-II] to D.S. and University Grant Commission to M.M. are highly appreciated. S.P. is thankful to UGC-MANF, New Delhi, for financial assistance.

Appendix A. Supplementary data

CCDC 915423 contains the supplementary crystallographic data for the complex. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.poly.2013.11.007.

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