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New insights into the bifunctionality of vanadium phosphorous oxides: A chemical switch between oxidative scission and pinacol rearrangement of vicinal diols

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ABSTRACT

New insights into the bifunctionality of vanadium phosphorus oxides (VPOs) were obtained. This study reports the precise tuning of experimental conditions, which act as the switch to direct the course of reaction selectively to obtain either C—C oxidative scission or an acid-catalysed rearrangement of vicinal diols. The catalyst was synthesized and characterized to identify the active vanadyl pyrophosphate phase. The present method was extended further to develop a new environmentally benign and green catalytic protocol for oxidative cleavage of a variety of vicinal diols with 100% selectivity towards the corresponding aldehydes or ketones using H_2O_2 as the oxidizing agent.

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1. Introduction

Vanadium-phosphorus oxides (VPOs) represent a class of redox catalysts of high commercial significance, due to their ability to induce selective oxidation of alkanes; in particular, for the synthesis of maleic anhydride from *n*-butane [1,2]. In fact VPOs are the only industrialized catalyst system used for oxidation of light alkanes [3–7]. The catalyst has been synthesized by numerous methods till date and extensively characterized using X-ray diffraction (XRD), N₂ adsorption, atomic emission, NH₃ Temperature-Programmed Desorption, and IR (Infra red), Raman, ³¹P NMR, XPS, LEIS and EPR spectroscopic techniques in order to understand the nature of active species [8]. VPOs exhibit rich and complex chemistry. Vanadyl pyrophosphate (VO)₂P₂O₇ has been widely accepted as the active and selective phase of this catalyst, however, a mixture of different V⁺⁴/V⁺⁵ phosphate phases are also observed resulting from a very easy redox cycle of V^{+4}/V^{+5} depending on the experimental conditions like reaction temperature, time-on-stream and redox properties of reactants [9-11]. The high efficiency of this catalyst has been attributed to its bifunctional nature containing redox sites as well as surface acidity. The redox nature of this catalyst has been ascribed to the availability and easy switching (reversible sequential reduction and re-oxidation) between different oxidation states of vanadium on catalyst surface (V⁺⁴/V⁺⁵). The surface acidity plays a crucial role in rate-determining step in the activation of paraffin and VPO catalysts are known to contain both Bronsted and Lewis acid sites in their structure [8,12]. Although oxidation catalysts based on VPOs are well established, their use as bifunctional acidic/redox catalysts has not been reported previously. Herein, we show that VPO based catalysts can be utilized as remarkably selective bifunctional catalysts with high activity using two exemplar reactions, the C–C oxidative scission of vicinal diols and acid-catalysed pinacol–pinacolone rearrangement of vicinal diols.

The oxidative scission of C–C bond in vicinal diols (vic-diols) to form corresponding aldehydes/ketones and carboxylic acids is a significant and most frequently employed tool in organic synthesis [13]. This reaction is very similar to many biochemical oxidative processes performed by redox enzymes, which possess a mononuclear iron-heme prosthetic group with additional cysteine or histidine residues, for instance the side chain cleavage of cholesterol catalysed by cytochrome P450 monooxygenase, and cleavage of arylglycerol-β-arylether linkages catalysed by the heme peroxidase ligninase [14,15]. Also the oxidative cleavage of vic-diol moieties in sugars has been used for preparation of chiral synthones [16]. Conventionally, this reaction has been carried out with high-valent inorganic oxidants; periodic acid and lead tetra acetate being the most common reagents [17,18]. In addition, the cleavage has also been studied with ceric ammonium nitrate, manganese dioxide, chromium trioxide,



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sodium bismuthate, NaIO₄-SiO₂, copper (II) bromide-lithium-tbutoxide [19-23]. However, such inorganic oxidants are required in high stoichiometric ratios and generate large volumes of inorganic by-products. In the past few years, in order to develop environment friendly methods, this reaction has been studied with heteropoly acid catalysts like Anderson-type polyoxometalate [Imo₆O₂₄]⁵⁻, ammonium molybdate, HPA with cetylpyridinium chloride as a phase transfer agent [24-27]. The reaction has also been studied with many organometallic complexes such as (dihydrogentellurato)-cuprate (III) and bis-(dihydrogentelluratoargentate (III) [28], iron (II) trisphenanthroline complex [29], cobalt acetyl acetone [30], Ru(PPh₃)₃Cl₂ on active carbon [31], tin porphyrin [32] and octahedral mononuclear manganese (III) complexes with tridentate equatorial ligand o-phenylenebis (oxamate)(opba)-dioxygen [33]. However, it is noteworthy that tedious experimental procedures are often employed for the preparation of such organometallic complexes.

In the course of our studies on pinacol rearrangement [34], we realized the versatility of diols, which can selectively form acidcatalysed rearrangement products under one set of conditions and oxidative cleavage products in presence of a powerful oxidant. This prompted us to investigate bifunctionality of VPO catalyst for this purpose. We report here for the first time the precise tuning of experimental conditions using VPO as selective bifunctional catalyst, which acts as a chemical switch to direct the course of reaction selectively to obtain either C–C oxidative scission or an acid-catalysed rearrangement of vic-diols. The present method was extended further to develop a new environmentally benign and green catalytic protocol for oxidative cleavage of a variety of vic-diols with 100% selectivity towards corresponding aldehydes or ketones using H_2O_2 as an oxidizing agent.

2. Materials and methods

2.1. Materials

All the chemicals were of reagent grade quality, and used as received. V_2O_5 and 85% H_3PO_4 were procured from s.d. fine chemicals Ltd., Mumbai. All the vic-diols were prepared according to literature procedures [35].

2.2. Preparation of catalyst precursor

VPO catalyst (with P/V ratio of 1.2:1) was synthesized by mixing an appropriate quantity of V_2O_5 and H_3PO_4 in isobutanol and refluxing at 105 °C for 3 h under N_2 atmosphere. The suspension obtained was cooled and the precipitate was filtered, washed with isobutanol and dried in a vacuum oven at 120 °C to yield VOHPO₄·0.5H₂O precursor [36]. Activation of VOHPO₄·0.5H₂O precursor was carried out to transform it into active catalyst. The precursor was calcined at 550 °C in nitrogen for 4 h to yield (VO)₂P₂O₇ which was used for the reactions.

2.3. Catalyst characterization

XRD (X-Ray diffraction analysis) of catalyst was carried out using Siemens D5000 diffractometer with Cu K_{\alpha} radiation, running at 40 kV/30 mA in the 2\theta range 10–80° with a step size of 0.05°. The IR spectra were recorded on a Perkin-Elmer 882 spectrophotometer as KBr pellets.

2.4. Oxidative cleavage of vic-diols (reactivity studies)

The reactions were carried out by mixing vic-diol (1 mmol) and required amount of catalyst in methanol as solvent at $60 \,^{\circ}$ C at atmospheric pressure in air. H_2O_2 was added dropwise using a

micro syringe. All reactions were monitored on TLC for complete consumption of starting compound. After completion, the reaction mixture was filtered to separate catalyst, and solvent was evaporated by distillation under reduced pressure to yield crude product. The purification was done by column chromatography using silica gel and using petroleum ether (60-80 °C)-ethyl acetate (6:4, v/v) as an eluent. The products were characterized by IR, ¹H NMR spectra, physical constants; and the data are in consonance with reported ones. The reaction was studied with respect to various parameters such as amount of catalyst, reaction time, nature of solvent, and use of co-oxidant.

3. Results and discussion

3.1. Synthesis and characterization of vanadyl pyrophosphate catalyst

The preparation procedure of this catalyst has a marked effect on its activity. Vanadyl pyrophosphate catalyst was prepared in organic medium using the reported procedure [37]. The method of catalyst preparation consisted of two steps; synthesis of the precursor, vanadyl hydrogen phosphate hemihydrate (VOHPO₄·0.5 H₂O), followed by subsequent dehydration to give active catalyst, vanadyl pyrophosphate (VO)₂P₂O₇. The active VPO catalyst, (VO₂)P₂O₇ with a P/V ratio of 1.2:1 was prepared by refluxing V₂O₅ and H₃PO₄ in isobutyl alcohol for 3 h. After filtration and washing, vanadium phosphate hemihydrate, VOHPO₄·0.5 H₂O was obtained, which was dried in vacuum at 120 °C to yield a catalyst precursor, VOHPO₄·0.5H₂O. The active catalyst phase, (VO)₂P₂O₇ was prepared by dehydration of VOHPO₄·0.5H₂O, by calcination in nitrogen

at 550°C for 4 h.2VOHPO₄ \cdot 0.5H₂O $\xrightarrow{\Delta}$ (VO)₂P₂O₇ + 2H₂O

The formation of catalyst precursor, VOHPO₄·0.5H₂O was verified by XRD and IR analyses. The XRD pattern of VOHPO₄·0.5.H₂O (Fig. 1a) showed very sharp characteristic peaks at 2θ values of 15.533 (001), 19.624 (101), 24.232 (021), 27.081 (121) and 30.484 (220); indicating a well-crystallized single phase [38]. It did not show presence of V₂O₅ phase indicating that all V₂O₅ has been consumed in the formation of new phase. It also confirmed the purity of VOHPO₄·0.5H₂O formed without any trace of impurity peaks. The IR-spectrum of VOHPO₄·0.5H₂O showed characteristic bands at 3375 and 1637 cm⁻¹ due to co-ordinated water (Fig. 2a). Further, the band at 1132 cm⁻¹ is due to the (P–OH) stretching of hydrogen phosphate group present in VOHPO₄·0.5H₂O. Bands



Fig. 1. X-Ray diffraction pattern of (a) VOHPO₄·0.5 H₂O and (b) (VO)₂P₂O₇.



Fig. 2. IR-spectrum of synthesized (a) VOHPO₄ \cdot 0.5 H₂O and (b) (VO)₂P₂O₇.

present in region 900–1200 cm⁻¹ can be attributed to P–O stretching [39].

The formation of active catalyst, vanadyl pyrophosphate, $(VO)_2P_2O_7$ was also verified similarly by XRD and IR analyses. The powder XRD pattern of catalyst showed characteristic peaks of $(VO)_2P_2O_7$ phase at 2θ values of 23.022 (200), 28.397 (013) and 29.867 (023) (Fig. 1b) [40]. The catalyst formed is fairly crystalline in nature. This is in accordance with the data reported in literature [39–41]. The IR-spectrum of synthesized ($VO)_2P_2O_7$ is shown in Fig. 2b. The band at 966 cm⁻¹ is assigned to V=O stretching in pyrophosphate structure. The bands at 1248, 1142, 1100 cm⁻¹ are attributed to stretching mode of $P_2O_7^{4-}$ group. All values are in agreement with reported values [39].

3.2. Catalytic activity of VPO catalyst in oxidative cleavage of vic-diols and acid catalysed rearrangement of vic-diols

The catalytic activity of VPO catalyst was tested in oxidative scission and acid catalysed rearrangement reaction of vic-diols. Preliminary studies were carried out using benzopinacol as model substrate in either methanol or benzene as solvent, under reflux conditions using VPO as catalyst. The reaction conditions were optimized with respect to various parameters like reaction temperature, amount of catalyst, choice of solvent and use of co-oxidant and a good control over the course of reaction was obtained. It was observed that choice of solvent played an important role in directing the course of reaction towards oxidative scission or acid catalysed rearrangement.

3.2.1. Effect of catalyst loading

The effect of catalyst loading was studied over a range of 0.1–2 mmol for 1 mmol of benzopinacol. Table 1 represents the effect of increasing catalyst loading on isolated yield of benzophenone in oxidative cleavage of benzopinacol (Table 1, entries 1, 2, 3). With an increase in the amount of VPO catalyst loaded, the yield of benzophenone increased linearly, along with the linear decrease in reaction time. However, a substantial loading of VPO catalyst was required to achieve high yield (>95%) of benzophenone. During the reaction, benzopinacol reduces the part of V⁺⁵ species to V⁺⁴ which cannot oxidize back to V⁺⁵ easily in the absence of oxidizing agent. As a result of this, although the reaction proceeds but it does not regenerate the V⁺⁵ species on the catalyst to close the redox cycle of V⁺⁵/V⁺⁴ species.

3.2.2. Effect of co-oxidizing agent

In order to improve the catalytic efficiency and decrease the catalyst loading, it is necessary to restore the V^{+5}/V^{+4} balance, by oxidizing the V^{+4} species to V^{+5} by using a co-oxidizing agent such as H_2O_2 . We selected H_2O_2 as an oxidant because of its easy availability, relative cheapness, and ability to act as a mild and selective oxidant. In addition, it produces water as by-product, and hence behaves as a green oxidizing agent. Benzopinacol cleavage was carried out with decreasing quantity of VPO in conjunction with H₂O₂. Thus, 1 mmol of benzopinacol in presence of 30% H₂O₂ (0.45 ml) effectively yielded 95% of product using as low as 0.1 mmol of VPO catalyst (Table 1, entries 4 and 5), increasing the VPO catalyst efficiency, decreasing reaction time and increasing the turnover frequency by 32 times than the use of equivalent or higher amount of VPO catalyst in the absence of H₂O₂, this indicates that the redox cycle of V⁺⁵/V⁺⁴ species is driving the reaction forward catalytically and stoichiometric amount of VPO catalyst is not required as was observed in the absence of H₂O₂ (Table 1, entries 1, 2, 3). All further studies were carried out in presence of H₂O₂ as an oxidant.

3.2.3. Effect of solvent

Solvents play an important role in the course of reaction as they can directly affect the product selectivity by interaction with the catalyst surface, blocking surface acidic sides as a function of increasing Lewis basicity, enhancing the reactant mobility or by changing the adsorption geometry of reactants on the surface of catalyst. Therefore, we decided to study effect of different solvents. Interesting trend was observed with various polar protic as well as aprotic solvents, and non-polar solvents, as shown in Table 2. It was seen that in case of polar protic solvents like, methanol, VPO catalyst efficiently catalysed the reaction showing maximum activity. In case of solvents, like acetonitrile and dioxane also, it showed good activity (Table 2, entries 5 and 6). Higher yields and cleaner reaction were obtained when methanol was used as a solvent as compared to 1,4-dioxane and acetonitrile. However, in case of non-polar solvents, like benzene and toluene in presence of H₂O₂ as oxidant at 60 °C, yield of benzophenone was as low as <20% (Table 2, entries 7 and 8). As observed above, solvent played a predominant role in VPO catalysed oxidative cleavage reaction. Amongst all the solvents studied, methanol was found to be most effective solvent to make VPO function as oxidation reagent. However, methanol being a protic polar solvent, its own involvement in reaction may be visualized, e.g. methanol may block the acidic centres of VPO catalyst, as methanol is a weak Lewis base. In order to throw more

Table 1	
Effect of catalyst loading.	

Entry	VPO catalyst (mmol)	Time (h)	30% H ₂ O ₂ (ml)	Yield of benzophenone [*] (%)	$TOF(h^{-1})$
1	0.65	5.5	-	71	0.198
2	1	4	_	80	0.2
3	2	1	_	96	0.48
4	0.1	1.5	0.45	95	6.4
5	0.32	1.5	0.45	96	2
6	No catalyst	4	5	-	-

Reaction conditions: benzopinacol = 0.4 g (1 mmol), MeOH = 20 ml, temperature 60 °C. Yields are of the isolated products.

Table 2

Oxidative cleavage of benzopinacol using VPO catalyst in presence of different solvents at 60°C.

Entry	Solvent	Time (h)	30% H ₂ O ₂ (ml)	Yield of benzophenone [*] (%)
1	MeOH	1.5	0.45	95
2	EtOH	1.5	0.6	90
3	IPA	2	0.77	87
4	t-BuOH	4	1.0	88
5	1,4-Dioxane	1.5	0.45	71
6	Acetonitrile	1	0.45	80
7	Benzene	5	0.45	19
8	Toluene	5	0.45	17

Reaction conditions: benzopinacol = 0.4 g (1 mmol), VPO catalyst = 0.032 g (0.1 mmol), solvent = 20 ml.

Reaction temperature = 60 °C, yields are of the isolated products.

light on role of methanol, we decided to carry out the reaction in a series of different primary, secondary and tertiary alcohols (Table 2, entries 2, 3 and 4). The general trend observed was that in case of secondary and tertiary alcohols, longer reaction time was required and comparatively more amount of H₂O₂ was consumed to bring about oxidative cleavage. The increase in the Lewis basicity of alcohols from 1° to 3° alcohol did not have any remarkable difference on the course of the reaction.

3.2.4. Switch over from oxidative cleavage to acid catalysed rearrangement

Oxidative cleavage of benzopinacol carried out in methanol as a solvent gave very high yield of benzophenone but as it can be seen in Table 2. entries 7 and 8. in benzene and toluene as a solvent the yield of benzophenone was very low \sim 20%. In order to know whether methanol plays any significant role in directing the course of reaction, we carried out the reaction in non-polar aprotic solvent benzene at its reflux temperature (Table 3). We observed that when a switch over was made from methanol to benzene, a change in the course of reaction was observed. In presence of benzene as a solvent, pinacol-pinacolone rearrangement of benzopinacol occurred selectively to form rearrangement product with 82% yield (Table 3, entry 2). In order to avoid carcinogenicity of benzene, we also attempted the reaction using toluene as a solvent at 80 °C and similar effect of acid-catalysed rearrangement was observed with similar yield as that in benzene (Table 3, entry 3). In benzene and toluene as reaction solvent, VPO functioned selectively as an acidic catalyst. Thus, we arrived at two sets of conditions - under one set, selective oxidative cleavage of benzopinacol occurred yielding benzophenone (in presence or absence of H_2O_2 as a co-oxidant); whereas, under second set, selective acid catalysed rearrangement occurred resulting in formation of benzopinacolone in high selectivity (Scheme 1).

3.2.5. C--C bond cleavage of vic-diols using VPO as bifunctional catalyst

Once the method was set, the conditions were successfully applied to bring about scission of C–C bond of a many different

Table 3

A switch over from oxidative cleavage of benzopinacol to acid catalysed rearrangement.



Reaction conditions: benzopinacol = 1 mmol, VPO catalyst = 2 mmol, reaction time = 1 h, solvent = 20 ml, reflux conditons.

Yields are of the isolated products.

substituted vic-diols. Most of the diols selected for the purpose were di-tertiary; however the reaction was also applied to secondary diols (Scheme 2). The results are shown in Table 4.

3.2.6. Reusability of recovered VPO catalyst

The reusability of this recovered VPO catalyst was established by carrying out repeated cycles of oxidative cleavage of benzopinacol with recovered catalyst (Table 5). At the end of a reaction, the catalyst was filtered, dried in air at 80 °C for 1 h, and reused in subsequent cycle. No make up quantity of catalyst was added during subsequent experiment. It was found that VPO catalyst could be effectively recycled without significant loss in catalytic activity (4 runs). ICP analysis of filtrate confirmed no leaching of V species

Table 4
Oxidative cleavage of different vic-diols using VPO-catalyst in MeOH at 60 °C

Entry	Substrate	Time (h)	30% H ₂ O ₂ (ml)	Product	Product yield [*] (%)
1	1a	1.5	0.45	2a	91
2	1b	1	0.5	2b	96
3	1c	1	0.5	2c	97
4	1d	2	0.7	2c	88
5	1e	3	0.7	2d	86
6	3a	1	0.5	4a	90
7	3b	1	0.5	4b	85
8	3c	1	0.5	4c	93
9	5a	0.5	0.5	6a	73
10	5b	0.5	0.5	6b	82

Reaction conditions: vic-diol = 1 mmol, VPO catalyst = 0.032 g (0.1 mmol), MeOH = 20 ml, temperature 60 °C.

Yields are of the isolated products.

Tabl



Scheme 1. Effect of change in reaction conditions on the course of the reaction.



Scheme 2. Products obtained in the oxidative cleavage of different vicinal diols.

Table 5

Reusability of VPO catalyst in oxidative cleavage of benzopinacol.

Entry	Run	Time (h)	30% H ₂ O ₂ (ml)	Yield of benzophenone [*] (%)
1	1	1.5	0.45	95
2	2	1.5	0.45	94
3	3	1.5	0.45	93
4	4	1.5	0.45	94

Reaction conditions: benzopinacol = 0.4 g (1 mmol), (VO)₂P₂O₇ = 0.032 g (0.1 mmol), MeOH = 20 ml.

* Yields are of the isolated products.

occurred. It was also seen that when catalyst was hot filtered at ${\sim}50\%$ conversion of benzopinacol, and reaction continued in the absence of solid catalyst, no further reaction occurred. Thus, VPO catalyst is re-usable for the oxidative cleavage of benzopinacol.

3.2.7. Mechanistic aspects

The plausible reaction mechanism of oxidative cleavage of vic-diols is shown in Scheme 3. On the basis of the observed experimental results, in the absence of co-oxidizing agent H_2O_2 , the reaction required substantial amount of VPO catalyst which is due to consumption of V⁺⁵ species being reduced to V⁺⁴ species. To establish the reaction mechanism, a control experiment with H_2O_2 alone, in the absence of VPO catalyst was performed, but no oxidative cleavage occurred, and almost 99% of starting compound was



Scheme 3. Proposed reaction mechanism for oxidative cleavage of vic-diols and regeneration of vanadium species in reaction mixture.

recovered back at the end of 4h, after consumption of substantial excess (5 ml) of H_2O_2 (Table 1, entry 6). Thus, a combination of VPO-H₂O₂ was essential for an efficient oxidative cleavage of vic-diols. The presence of co-oxidizing agent H₂O₂ was essential to restore the balance of V^{+5}/V^{+4} species. The oxidative cleavage in presence of VPO catalyst is thought to involve a reversible V⁺⁵/V⁺⁴ redox cycle. Similar redox mechanism was also observed in the allylic oxidation of cyclohexane using VPO catalyst in presence of tertiary butyl hydroperoxide as co-oxidant [42]. Based on our experimental results and the mechanism reported in literature, the reaction pathway for oxidative scission of benzopinacol is shown in Scheme 3. In this scheme, when benzopinacol undergoes oxidative scission, a part of V⁺⁵ species was reduced to V⁺⁴ species, which was oxidized back to V^{+5} species in presence of H_2O_2 to complete the redox cycle. The (P:V) ratio in synthesized (VO)₂P₂O₇ catalyst was (1.2:1), the excess of phosphorus present on catalyst surface stabilizes pyrophosphate framework and regenerates V⁺⁵ sites, which were essential to V^{+4}/V^{+5} redox mechanism.

In benzene and toluene as reaction solvent, VPO selectively functioned as an acidic catalyst with the formation of benzopinacolone in high selectivity. The pinacol–pinacolone rearrangement is proposed to proceed through acid catalysed elimination mechanism. It is envisaged that the OH groups of pinacole are probably coordinated onto the V⁵⁺ site of VPO through oxygen atoms, while the H atoms on the hydroxyl groups may be stabilized by hydrogen bonding with lattice oxygens of VPO to form acidic protons which can easily transfer to the vicinal OH group in the pinacol molecule. The V–O bond in adsorbed pinacol molecule stabilizes the carbenium ion intermediate formed by the dehydration of coordinated pinacol. The back-donation of electron pair from V–O bond to C–O bond facilitates the formation of a pinacolone through the migration of methyl group. The pinacolone molecule is easily removed by the solvent to regenerate the catalytic active site.

4. Conclusions

In conclusion, oxidative cleavage of vicinal diols is reported for the first time in presence of VPO catalyst, using H_2O_2 as an oxidant. The catalyst displayed excellent activity. Bifunctionality of vanadyl pyrophosphate catalyst is very prominently exhibited in selectively bringing out the oxidative cleavage of vic-diols giving corresponding aldehydes/ketones or an acid-catalysed rearrangement product depending on the choice of solvent. The protocol was successfully extended to variety of ditertiary as well as secondary diols to yield aldehydes and ketones selectively. The carbonyl compounds were obtained in high isolated yields without over oxidation to acids. The amount of catalyst used to induce the cleavage is catalytic with respect to substrate molecule. The VPO catalyst can be recycled efficiently without any loss in catalytic activity. The catalyst regeneration mechanism has been proposed.

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