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Multiple Oxo-Vanadium Schiff Base Containing Cyclotriphosphazene as a Robust Heterogeneous Catalyst for Regioselective Oxidation of Naphthols and Phenols to Quinones

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Abstract Grafting of multiple oxo-vanadium Schiff base moieties to cyclotriphosphazene provided an efficient and recyclable heterogeneous catalyst for the regioselective oxidation of naphthols and phenols to quinones by using *t*-butylhydroperoxide as oxidant. One of the main advantages of the developed catalyst was the presence of multiple oxo-vanadium moieties in close proximity which made the developed catalyst more active as compared to its homogeneous oxo-vanadium Schiff base. After the reaction, the catalyst was easily recovered from the reaction mixture by simple filtration and reused for five runs without loss in activity.

Keywords Cyclotriphosphazene · Vanadium · Oxidation · Naphthol · Quinone

1 Introduction

Recent trend in the evolution of environmentally benign synthesis has evoked considerable interest in developing reusable metal catalysts and reagents that maintain high activity, selectivity and facile recovery of the catalyst [1, 2]. As transition metal complexes are often expensive to purchase or prepare, making them recyclable offer several advantages such as simplicity in handling, facile recovery from reaction mixture and reusability. Cyclophosphazenes are a remarkable class of inorganic compounds which have found extensive uses in the development of polymeric materials intended for a variety of commercial applications [3, 4]. The synthetic utility of cyclotriphosphazenes is mainly due to the presence of reactive halogens and their ease of nucleophilic substitution [5]. Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$), a readily available starting material, is used increasingly for the synthesis of functionalized dendrimers and macrocyclic compounds by nucleophilic substitution of chlorine with number of potential donor ligands [6–8]. Nevertheless, few derivatives containing silicon substituents have been reported in the literature [9–11], metal containing derivatives of cyclotriphosphazenes are scarcely reported [12]. We have previously reported [13] the application of cyclotriphosphazene grafted silica for immobilizing the oxo-vanadium Schiff base moieties for hydroxylation of benzene. The developed catalyst was found to be highly active than its corresponding oxo-vanadium Schiff base, probably due to the presence of multiple organometallic anchored fragments on close proximity. Inspired with our own results, we targeted to explore the applications of cyclotriphosphazenes for linking of the organometallic moieties.

Regioselective oxidation of naphthols and phenols to quinones is an important reaction as quinones are versatile and highly useful compounds as synthetic intermediates as well as biologically active compounds. Some quinones show bioactivities and are used as medicine intermediates. For example, trimethyl-p-benzoquinone is a key compound in the vitamin E synthesis, and 2-methyl-1,4-naphthoquinone is used as blood coagulating agent and as supplement in animal food [14–16]. Although, oxidation of naphthols and phenols to the corresponding quinones is well documented in the literature [17–19], the scope for developing an efficient and recyclable catalyst for this valuable reaction is still remained. In continuation to our work on development of new synthetic methodologies [20–24], we herein report an efficient catalytic approach for the

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regioselective oxidation of naphthols and phenols to corresponding quinones using *tert*-butylhydroperoxide as the sole oxidant in the presence of multiple oxo-vanadium schiff base conatining cyclotriphosphazene as catalyst.

2 Experimental

2.1 Material

All chemicals, solvents, and reagents were of reagent grade quality and were used as purchased from commercial sources. All solvents were dried and purified before use. Oxo-vanadium Schiff base **1** was prepared by following the literature procedure [25].

2.2 Measurements

FT-IR spectra were obtained on a Perkin Elmer FTIR X 1760 spectrophotometer with the samples prepared as KBr pellets. ^{1}H and ^{13}C NMR Spectra were recorded on a Bruker Avance 300 Spectrometer in $CDCl_3$. Elemental analysis was done by using ASTM D-3828 (Kjeldhal method). Analysis for metal contents were carried out by using inductively coupled plasma atomic emission spectrometer (ICP-AES, PS-3000UV) by Leeman Labs.

2.3 Preparation of Multiple Oxo-Vanadium Schiff Base Containing Cyclotriphosphazene 3

To a stirred solution of vanadium Schiff base **1** (1.84 g, 4.0 mmol) in dry DMF (15 ml) was added NaH (0.24 g, 10 mmol) at 0 °C in one portion and the mixture was slowly warmed to room temperature. After stirring for 30 min at room temperature, hexachlorocyclotriphosphazene **2** (0.34 g, 1.0 mmol) was added and the resulting mixture was vigorously stirred and heated for 8 h at 80 °C. After being cooled to room temperature, the black solid thus obtained was separated by filtration and washed with DMF, water, methanol and dried under vacuum. Yield 1.65 g (94 %). IR (cm^{-1}): 2924, 2656, 1654, 1600, 1383, 1292, 1207, 1146, 982; Analytical data: C 30.31 %; H 4.64 %; N 11.48 %; Cl 2.58 %.

2.4 General Experimental Procedure for the Oxidation of Naphthols and Phenols

To the stirred mixture of naphthol or phenol (1 mmol), anhydrous TBHP (5–6 M solution in decane; 2 mmol) in acetonitrile (3 ml) was added catalyst **3** (1 mol%, 0.01 mmol). The resulting mixture was heated at 70 °C for the time reported in the Table 1. Progress of the reaction was monitored by TLC. After completion, the catalyst was separated by filtration and washed with dichloromethane and dried under vacuum for further use. The filtrate was concentrated under reduced pressure and residue so obtained was dissolved in dichloromethane (10 ml). The organic layer was washed with water (2 × 15 ml), dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to give corresponding oxidized product. The conversion of the products was determined by GCMS and selectivity was determined by ^{1}H NMR.

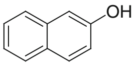
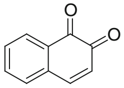
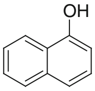
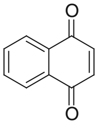
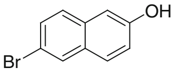
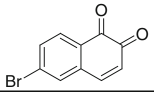
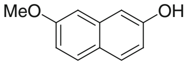
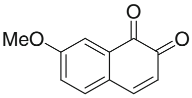
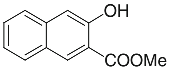
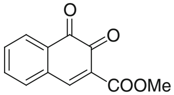
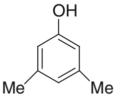
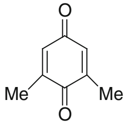
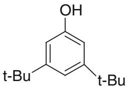
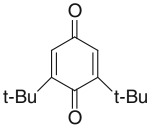
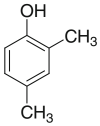
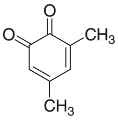
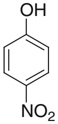
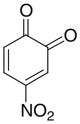
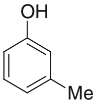
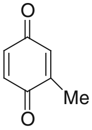
3 Result and Discussion

3.1 Synthesis and Characterization

The synthetic route of the multiple oxo-vanadium Schiff base containing cyclotriphosphazene **3** is shown in Scheme 1. The required oxo-vanadium Schiff base **1** was readily prepared by the reaction of 4-hydroxysalicylaldehyde, 2-aminoethanol and vanadyl acetylacetonate by following the literature procedure [25]. The reaction between oxo-vanadium Schiff base **1** and hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) **2** in a molar ratio (6:1) in dry DMF at 80 °C resulted in the formation of dark brown colored solid, which was precipitated out on cooling. The precipitated cyclotriphosphazene containing oxo-vanadium Schiff base **3** was isolated by filtration. The solid thus obtained was washed several times with DMF, hot methanol and dried under vacuum.

The synthesized catalyst was characterized by the IR, elemental analysis and TGA. The catalyst **3** exhibits a intense IR band at 982 cm^{-1} characteristic to the V=O and strong bands in the region of 1,150–1,215 cm^{-1} corresponding to cyclotriphosphazene structure, confirming the covalent attachment of complex **1** to the cyclotriphosphazene support **2**. In addition disappearance of phenolic band (3,200–3,400 cm^{-1}) and lower shift of a band from 1,631 to 1,600 cm^{-1} corresponding to C=N of the Schiff base further revealing the formation of heterogenized complex **3.** Since, the displacement of all the chloro groups by oxo-vanadium Schiff base moieties to form a condensed structure as **3** is difficult, thus we assumed that the obtained heterogeneous material might be containing structural units having different number of oxo-vanadium Schiff base moieties attached to the cyclotriphosphazene molecule. We performed the synthesis of catalyst in DMF, thus attachment of solvent molecules to metal centre is obvious, which is further confirmed by the presence of an intense band at 1749 cm^{-1} in IR. Furthermore, we analyzed the prepared material by elemental analysis and the observed percentage of chlorine (2.58 %) and nitrogen (11.48 %) suggested the structure of the prepared material as

Table 1 Oxidation of naphthols and phenols with *t*-butylhydroperoxide[a]

Entry	Substrate	Product	Time (h)	Conv. (%)*	Yield (%)[b]
1			4.0	85 70	78 15[c]
2			3.5	80	74
3			5.5	70	66
4			4.5	72	68
5			6.5	60	57
6			3.0	92	88
7			2.5	94	90
8			2.5	92	87
9			8.5	40	30
10			3.0	90	86

*Conversion determined by HPLC and GCMS and selectivity of the products was confirmed by ^{1}H NMR

[a] Reaction conditions: substrate (1 mmol), TBHP in decane (2.0 mmol), catalyst **3** (1 mol%), acetonitrile (3 ml) at 70 °C

[b] Isolated yield

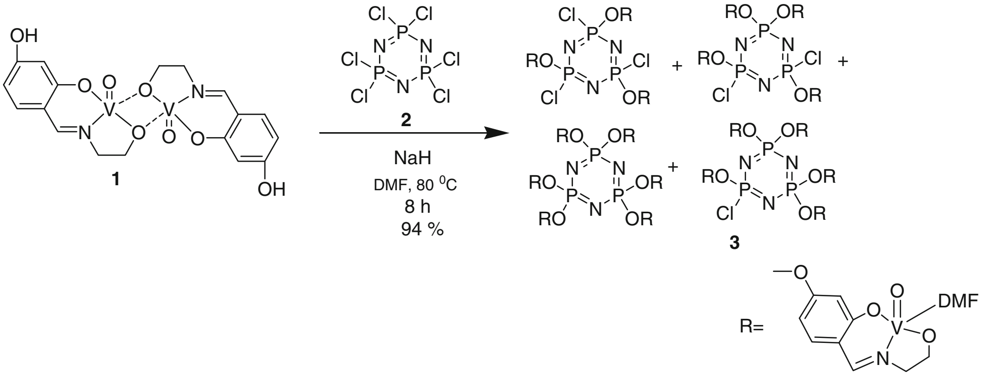
[c] Using homogeneous oxo-vanadium complex **1** as catalyst, resulting the mixture of 4,4′-binaphthol and 1,2-naphthoquinone

$N_3P_3Clx[VO(Schiff\ base)dmf]_{6-x}$ **3**. The percentage of vanadium in the supported catalyst was determined by thermogravimetric (TGA) analysis under oxygen atmosphere. The prepared catalyst was found to be stable thermally up to ca 150 °C and started losing weight between 150 and 200 °C due to the loss of coordinated solvent molecules. Further the weight loss was observed at different stages at different temperatures between 300 and 500 °C, probably due to the decomposition of the part of ligand moiety and phosphorus structure. Finally sublimation with 40 % residue at 750 °C suggested the formation of V_2O_5 at the end which corresponds to the 12.5 % percentage of vanadium in the supported catalyst **3.** In the mass spectrum of **3**, the presence of molecular ion peak at m/z 1,493, suggested the proposed structure as shown in Scheme 1.

3.2 Catalytic Studies

3.2.1 Oxidation of Naphthols and Phenols with Catalyst 3

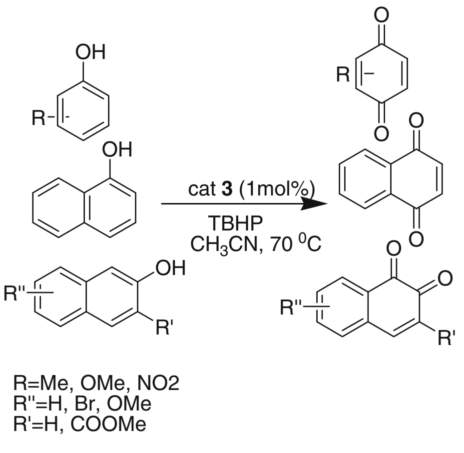
The prepared catalyst **3** has been used for the oxidation of napthols and phenols using anhydrous *t*-butylhydroperoxide (solution in decane) as oxidant (Scheme 2). Simple



Scheme 1 Synthetic route of catalyst **3**

mixing of the 2-naphthol (1 mmol) and catalyst **3** (1 mol%) in presence of anhydrous TBHP (2 mmol) in acetonitrile at 70 °C allowed the convenient and high yielding oxidation to *o*-naphthoquinone. After completion of the reaction as monitored by TLC analysis, the catalyst was separated by filtration and reused as such for subsequent runs. The filtrate was subjected to the usual workup to give the corresponding oxidized product. Importantly, the leaching of metal or ligand was not detected in this course, which was ascertained by subjecting the filtrate sample and product to ICP-AES analysis.

The development of synthetic methodologies for the oxidation using molecular oxygen, hydrogen peroxide as oxidants is important both from environmental and economical viewpoint. Keeping this in view, we also performed the oxidation of 2-naphthol by using molecular oxygen as oxidant under similar reaction conditions. The reaction did not take place even after prolonged reaction time. However, the use of hydrogen peroxide as oxidant affected the selectivity of reaction adversely and yielded an intricate mixture of the products. This is probably due to the non-productive decomposition of hydrogen peroxide by vanadium catalyst. Therefore, we have chosen *t*-butylhydroperoxide as an optimum oxidant for the present transformation. In a controlled experiment, the oxidation of 2-naphthol with TBHP in the absence of catalyst was not occurred even after prolonged reaction time (6 h). The reaction was found to be slow at room temperature, however 70 °C was found to be optimum for this reaction. Further increase in reaction temperature did not improve the results to any significant extent.



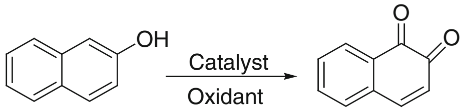
Scheme 2 Oxidation of naphthols and phenols to quinones

Further we studied the oxidation of various naphthols and phenols under similar reaction conditions. The results of these experiments are presented in Table 1. All the substrates were efficiently converted to corresponding quinones selectively without any evidence for the formation of coupling product. The reaction times varied from 2.5 to 8.5 h, depending upon the functional groups substituted on the starting substrate. The reaction was failed in case of unsubstituted phenol, however, substituted phenols and 1-naphthol, were selectively converted to *p*-quinones in good to excellent yields (Table 1, entries 2, 6–7). However, in case of 2,4-dimethyl phenol, 4-nitrophenol and 2-naphthols, where *p*-position was blocked, the reaction favoured the synthesis of the corresponding *o*-quinones selectively (Table 1, entries 1, 3–5, 8, 9). As, *p*-isomers are more stable and symmetric than *o*-isomers, therefore, thus the reactions favours the regioselective synthesis of 1,4-quinones in most of the phenolic substrates.

To evaluate the effect of solvent, we studied the oxidation of 2-naphthol under described reaction conditions by using different solvents such as acetonitrile, toluene, dichloroethane. Among the various solvents studied, acetonitrile was found to be solvent of choice from conversion and reaction time points of view. In case of toluene and dichloromethane, the reaction was found to be very slow and provided very poor yield of the desired product.

We also compared the catalytic potential of the heterogeneous catalyst **3** with the corresponding homogeneous

Table 2 Comparison of catalyst **3** with other reported catalysts



Entry	Catalyst	Reaction time (h)	Yield (%)	Ref.
1	Cyclotriphosphazene linked oxo-vanadium Schiff base **3**	4.0	85[a]	–
2	IBX (o-iodoxybenzoic acid)	10.0	84	19
3	$Rh_2(cap)_4$	4.0	57[b]	26
4	$PhIO_2$ in AcOH	12 0	65	27
5	Polymer supported vanadium salt	12	65	28
6	Martin's reagent	12	87	29
7	Heteropolytungstate	1.0	83[b]	30
8	Vanadium-substituted Keggin heteropolyacid	–	75[b]	31

[a] GC yield

[b] Isolated yields

oxo-vanadium Schiff base **1** by performing the oxidation of 2-naphthol under similar reaction conditions. The cyclotriphosphazene linked oxo-vanadium **3** was found to be more efficient and selective catalyst, which yielded 1,2-naphthoquinoe exclusively. Whereas in case of catalyst **1,** the reaction was found to be slow and yielded poor yield of the desired product along with the formation of 4,4′-binaphthol as by-product (Table 1, entry 1). Enhanced catalytic activity of the catalyst **3** in comparison to catalyst **1**, is probably due to the presence of multiple oxo-vanadium moieties in close proximity to the cyclotriphosphazene support.

The comparison of cyclotriphosphazene grafted oxo-vanadium Schiff base **3** with the reported catalysts by considering the oxidation of 2-naphthol to *o*-naphthoquinone as model substrate is shown in Table 2. The higher yield, enhanced selectivity and lower reaction time with the added benefits of facile recovery and recycling ability of catalyst noticeably reflects the superiority of the developed catalyst **3** over existing methods.

Furthermore, recycling of the catalyst was tested by performing the oxidation of 2-naphthol with TBHP under described reaction condition. After completion of the reaction, the catalyst was easily recovered from the reaction mixture by simple filtration and reused as such for subsequent runs. As shown in Fig. 1, the developed catalyst showed consistent catalytic activity for five runs and afforded similar yield of the desired product. Last but not least, we also checked the leaching of the metal or ligand from the catalyst by refluxing the catalyst **3** in acetonitrile for 3–4 h. The catalyst was separated by filtration and filtrate so obtained was charged with oxidant and 2-naphthol. The reaction was continued for 6 h under described reaction conditions. No reaction was observed; confirming that there was no leaching occurred during the reaction and therefore the reaction was truly heterogeneous in nature.

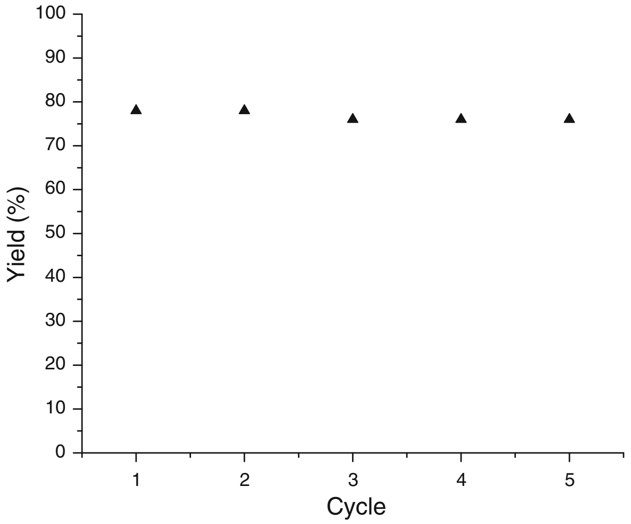


Fig. 1 Result of recycling experiments

4 Conclusion

In conclusion, we have demonstrated an efficient multiple oxo-vanadium Schiff base containing cyclotriphosphazene catalyst for the regioselective oxidation of the naphthols and phenols to corresponding quinones by using *t*-butylhydroperoxide as oxidant. The advantageous features of the developed catalyst are its facile synthesis, higher catalytic activity, regioselective nature and recycling ability without significant loss in catalytic activity. Because of the unique chemistry of cyclotriphosphazenes, we believe that the present report will open a wide scope in developing new catalytic materials/methodologies for organic transformations.

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