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of

[VO(PS-BBMA)](SO₄) catalyzed α-oxygenation of benzylamines to amides in solvent free condition

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Abstract

Polymer anchored [VO(PS-BBMA]SO₄ and unsupported [VO(BBMA]SO₄ catalysts were synthesized and characterized by elemental analyses, FT-IR, ESR, UV–vis diffuse reflectance spectroscopy (DRS), thermogravimetric analysis (TGA), and vibrating sample magnetometry (VSM). A protocol for the synthesis of benzamides from benzylamine has been developed using [VO(PS-BBMA]SO₄ as a effective catalyst under solvent free conditions in presence of H_2O_2 . The reactions provide good yields of the corresponding amide products with substrate scope and excellent functional group compatibility. The developed catalyst can be facilely recovered, heterogeneous, compared with unsupported analogue and reused six times without significant decrease in its activity.

Keywords: α -oxygenation, benzyl amine, H₂O₂, benzamide, [VO(BBMA]SO₄, [VO(PS-BBMA]SO₄

1. Introduction

Oxidation of amines to amides is an important reaction because amides are valuable synthetic intermediates in chemistry as well as in biology. Amides are widely used in the synthesis of peptide and proteins, intensifiers of perfume, anti-block reagents, color pigments for inks, detergents and lubricants [1, 2]. Methacrylamide and caprolactum are two amide group-containing monomeric compounds of great industrial relevance in the preparation of polymers [3]. Compounds of amides are known to have excellent anthropod-controlling activity and applications in treatment of HIV disease, cardiovascular disease, hypertension and high blood pressure [4] and also found in polymers, fine chemicals, pharmaceuticals, and natural products [5]. The traditional synthetic approach used for amide formation involves the reaction of an amine with activated carboxylic acid derivatives [6] or coupling with carboxylic acids mediated by coupling reagents [7, 8], which suffers from several common drawbacks such as the use of highly hazardous reagents, harsh reaction conditions,

toxicity issues, poor atom-efficiency, and generation of wastes that not only reduce process efficiency but also pose environmental problems. This necessitates the development of efficient methods for amide bond formation that circumvents these problems. To address these challenges in amide synthesis, a plethora of novel amide formation reactions have been developed [9, 10], such as catalytic acylation of amines with carboxylic acid [11, 12], dehydrogenative amidation of alcohol [13-15], amino carbonylation of haloarenes [16-18], hydroamination of alkynes [19, 20], transamidation of primary amides [21-24], and oxidative amidation of aldehydes [25-29]. Direct oxygenation of primary amines to primary amide by molecular oxygen was reported in presence of water and ruthenium hydroxide supported on alumina catalyst [30]. Tanaka et al. [31] reported amine group was protected with tert.-butoxycarbonylgroup (Boc) and then oxygenated using in situ generated RuO₄ followed by deprotection of the Boc group. There are only a few reports in the literature regarding the oxidation of amines [32].

Amines are desirable starting materials for the synthesis of amides because they are readily available and inexpensive. The oxidation of benzylamine is reported over [VO(PS-BBMA]SO₄ catalyst with oxidant. Vanadium complexes play a very important role in catalytic organic synthesis because hydroxyl radicals are very efficiently generated from H_2O_2 under the action of vanadium catalysts [33]. Benzylamine can be converted into benzamide using this catalyst (Scheme 2). A remarkable feature is that the process was carried out in the absence of base, solvent or any other external additives which makes the process environmental benign.

2. Experimental

2.1. Materials and methods

Chloromethylated polystyrene divinyl benzene (PS) was obtained as a gift from THERMAX Ltd. India. The $VOSO_4$, *o*-phenylenediamine, iminodiacetic acid, benzylamine, substituted benzyl amines, H_2O_2 were purchased from Merck and used without further purification. Solvents were used after purification by standard methods.

Elemental analyses were carried out using an Elementar Vario Micro Cube CHNS analyzer. Ultraviolet-visible light (UV-vis) reflectance spectra of the solid samples were recorded on a Shimadzu UV-Vis-NIR model-3101P spectrophotometer, with reference to non-absorbing BaSO₄ as a standard. IR spectra were recorded in KBr on Shimadzu 8,400 s spectrometer in the range 4000-400 cm⁻¹. Thermogravimetric analyses was carried out with a TA instrument, SDT

analyser model Q600. ESR measurements of solid sample at room temperature in a standard X band JES - FA200 spectrometer. The vanadium content was determined by using atomic absorption spectrometer, after destruction of the complexes with concentrated H_2SO_4/H_2O_2 mixture by using Avanta Pm, GF 3000. Molar conductivity measurements were carried out by using a WTW conductivity meter. LCMS measurements were recorded on a LC-MSD-Trap-XCT-Plus. Magnetic moment of the complex was measured by a VSM model 7404 at IIT Madras. Nuclear magnetic resonance spectra were recorded on 400 MHz Bruker Avance spectrometer using TMS as standard in CDCl₃ solvent. Spin multiplicities are described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet) and br s (broad singlet).

2.2. Preparation of unsupported vanadium complex [VO(BBMA)]SO₄

The unsupported complex [VO(BBMA)]SO₄ was synthesized by mixing aqueous solution of VOSO₄.5H₂O (1.5 g, 10 mmol) and BBMA in methanol 1:1 molar ratio (1.1 g, 10 mmol) and stirred for 24 h. The grey colored compound was filtered, Soxhlet extracted with ethanol and dried in the oven for 12 h. Yield: 2.1 g; 75 %.

2.3. Preparation of polymer supported vanadium complex [VO(PS-BBMA)]SO4

Bis(benzimidazol-2-ylmethyl)amine (BBMA) was synthesized according to the procedure described in the literature [34]. Chloromethylated polystyrene (1.0 g, Cl content 6 mmol) was swelled in DMF for 2 h, and then a solution of BBMA (0.29 g, 0.78 mmol) in DMF (10 mL) was added, followed by triethylamine (4 mL) and ethyl acetate (30 mL). The mixture was heated at 100 °C for 48 h. After cooling, it was filtered, Soxhlet extracted with ethanol, and dried. 1.0 g of functionalized polymer (PS-BBMA) was added to water (10 mL) and kept for 1 h. A solution of VOSO₄.XH₂O (0.23 g; 1 mmol) in water (10 mL) was added to it and the mixture was stirred at RT for 24 h. The resultant grey coloured beads were filtered off and washed by Soxhlet extraction and dried at 100 °C (Scheme 1).



Scheme 1. Synthesis of [VO(PS-BBMA)]SO₄

2.4. General protocol for synthesis of amides

Benzylamine (0.214 g, 2.00 mmol), [VO(PS-BBMA]SO₄ (80 mg, 0.08 mmol) and H₂O₂ (4 mmol) was heated at 80 °C for 10 h in a round bottom flask under nitrogen atmosphere. The reaction was monitored by TLC, and after complete consumption of benzylamine, the reaction mixture was cooled to room temperature, filtered and concentrated in vacuo. The residue was purified by column chromatography (ethyl acetate: hexane = 1:8) to afford benzamide. The product was analyzed by ¹H NMR spectroscopy.

3. Results and discussion

3.1. Characterization of [VO(PS-BBMA)]SO₄ and [VO(BBMA)]SO₄

3.1.1. CHN, molar conductance and AAS

Polymer beads were functionalized with BBP, followed by the reaction with VOSO₄.H₂O to yield the complex [VO(PS-BBMA)]SO₄. Elemental analysis showed that the functionalized BBP has 5.1 % nitrogen content, which indicated that the successful functionalization of the polymer. Metal estimation by AAS indicated 5.1 and 10.8 % of V in the polymer supported and unsupported vanadium catalysts respectively (Table 1). The molar conductance value of unsupported complex was 69 ohm⁻¹ cm² mol⁻¹ in DMF its indicated 1:1 electrolytic nature.

Table 1

Elemental analyses of PS, BBMA, PS-BBMA, [VO(PS-BBMA)](SO₄) and [VO(BBMA)](SO₄)
CHN analyses (%)

| | CHN analyses (%) | | | | | |
|---------------------------------|------------------|--------|-------|--------|--|--|
| Compound | С | Ν | Н | V | | |
| BBMA | 70.1 | 23.1 | 6.8 | - | | |
| PS | 97.8 | - | 2.2 | - | | |
| PS-BBMA | 90.7 | 5.2 | 4.1 | - | | |
| [VO(PS-BBMA)](SO ₄) | 75.1 | 7.0 | 8.3 | 5.1 | | |
| [VO(BBMA)](SO ₄)* | 41.1 | 14.9 | 2.9 | 10.8 | | |
| 4 | (43.7) | (15.9) | (3.2) | (11.6) | | |

*Calculated values are in parentheses

3.1.2. FT-IR analyses

The IR spectrum of the PS exhibited peaks at 1,267 and 829 cm⁻¹ due to vCH₂-Cl and vC–Cl (Table 2, Fig. S1). On functionalization, these bands decreased in intensity, indicating the bonding of BBMA onto the polymer support. The free BBMA exhibited a band around 3056 and 3010 cm⁻¹ corresponding to ArN–H and aliphatic N-H group (Fig. S2) whereas later peak was absent in the functionalized polymer (Fig. S3), as the bonding of the ligand to the polymer beads is accomplished through the aliphatic nitrogen. The functionalized beads exhibited a band at 1580 cm⁻¹ due to vC=N, which was shifted to 1508 cm⁻¹ in the anchored beads, indicating that the nitrogen atoms of the pyridine and benzimidazole moieties of the ligand are coordinated to vanadium (Fig. S4). The unsupported complex exhibited bands at 3202, 3121, 1628 cm⁻¹ due to vArN–H, vN–H and vC=N respectively (Fig. S5). Both supported and unsupported complexes exhibited bands in the range 1100-1200 and 600-630 cm⁻¹ due to v₃ and v₄ of sulphate outside the coordination sphere [35].

Table 2

FTIR spectral data of PS, BBMA, PS-BBMA, [VO(PS-BBMA)](SO₄) and [VO(BBMA)](SO₄)

| | IR spectral data v(cm ⁻¹) | | | | | | |
|---------------------------------|---------------------------------------|---------|-------|------|------|--|--|
| Compound | CH ₂ -Cl | C-Cl | ArN-H | N-H | C=N | v ₃ (SO ₄) | v ₄ (SO ₄) |
| BBMA | - | - | 3056 | 3010 | 1583 | - | - |
| PS | 1267 (s) | 829 (s) | - | - | - | - | - |
| PS-BBMA | 1267(w) | 829(w) | 2924 | - | 1580 | - | - |
| [VO(PS-BBMA)](SO ₄) | - | - | 2923 | - | 1508 | 1200 | 620 |
| [VO(BBMA)](SO ₄) | - | - | 3202 | 3121 | 1628 | 1168 | 612 |

3.1.3. Electronic spectral studies

The electronic spectra of [VO(PS-BBMA)](SO₄) (Fig. 1) and [VO(BBMA)](SO₄) (Fig. S6) complexes exhibited strong absorption bands in the region 206 to 300 nm due to $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of BBMA and PS. The electronic spectra of both the complexes showed bands around 448, 530, 700 nm and 425, 540 and 745 nm, which are assigned to ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$, ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ and ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transitions [36] of [VO(PS-BBMA)](SO₄) and [VO(BBMA)](SO₄) respectively having V(IV) with d¹ configuration in a distorted tetrahedral geometry respectively.



Fig. 1. Electronic spectrum of [VO(PS-BBMA)](SO₄)

3.1.4. TGA studies

Thermogram of $[VO(BBMA)](SO_4)$ (Fig. S7) displayed first weight loss in the range 170-223 °C which corresponds to the loss of sulphate. Further weight loss (60 %) was observed between 223 and 465 °C due to the loss of BBMA. The thermal decomposition of $[VO(PS-BBMA)](SO_4)$ proceeded in two stages (Fig. S8), weight loss of 10 % from 200-240 °C, which could be attributed to sulphate group, 22 % weight loss in the range 240-325 °C due to loss of BBMA, whilst above 325 °C due to decomposition of polymer occurred. In conclusion, the polymer supported oxovanadium complex is more stable compared to its homogeneous analogue.

3.1.5. EPR and magnetic moment measurements

The X-band EPR spectra of [VO(BBMA)](SO₄) (Fig. S9) and [VO(PS-BBMA)](SO₄) (Fig. 2) recorded in the solid state at room temperature. The spectrum showed two types of resonance components, one set due to the parallel peaks and the other set due to perpendicular peaks which indicates axially symmetric anisotropy with sixteen line hyperfine splitting, characteristic of interaction between electron and vanadium nuclear spin.

Room temperature magnetic moments of $[VO(BBMA)](SO_4)$ and $[VO(PS-BBMA)](SO_4)$ were measured using a vibrating sample magnetometer. They exhibited a value of ~1.74 BM, which was very consistent with the expected spin-only magnetic moment S = $\frac{1}{2}$, d¹ vanadium(IV) system.



Fig. 2. X-band ESR spectrum of [VO(PS-BBMA)](SO₄)

3.1.6. LCMS Studies

For $[VO(BBMA)](SO_4)$, the molecular ion peak was found at m/z 343.2 with 4.2 retention time due to the cationic ion $[VO(BBMA)]^{2+}$ (Fig. S10).

Based on the above results, tetrahedral geometry was suggested for both polymer anchored and unsupported V(IV) complexes.

3.2. Catalytic activity

Initially, benzylamine oxidation was chosen as model substrate to optimize the reaction conditions with $[VO(PS-BBMA]SO_4 \text{ catalyst.} Some screening results are summarized in Table 3. The reaction proceeded successfully in solvent free conditions. Hence, temperature, substrate to oxidant ratio and catalyst concentration was varied.$

The reaction proceeded well at 70 °C with the yield of 90 % (Table 3) and at 80 °C, the reaction reached the highest yield of 92 % and with further increase in temperature, the conversion slightly decreased (entry 3). Therefore, the temperature of 80 °C was selected for further exploration. Further, oxidants screening showed that H_2O_2 as oxidant in the reaction gave 92 % yield (Table 3, entry 2) while using oxidants O_2 and TBHP, the reaction gave very low yield (42 and 63 %) (Table 3, entry 9 and 8). Effect of [VO(PS-BBMA]SO₄ concentration was investigated with 1:2 molar ratio of benzylamine: H_2O_2 , 2 mmol of the benzylamine for 10 h at 80 °C. It was found that with 80 mg (0.08 mmol) of catalyst (Table 3, entry 2) the reaction gave 92 % yield. At lower concentration (70 mg, 0.07 mmol), 72 % yield was obtained. Increase in catalyst concentration to 90 mg (0.09 mmol), the conversion was same. Hence 80 mg of [VO(PS-BBMA]SO₄ was chosen as the optimum catalyst concentration.

When the reaction was carried out with 2 mmol of benzylamine, 80 mg of [VO(PS-BBMA]SO₄ with 1:1 ratio of benzylamine and H_2O_2 ratio concentration for 10 h at 80 °C, the reaction was slow with only 50 % conversion (entry 4). Further increase in the ratio to 1:2, the yield was 92 % (entry 2). When the benzylamine: H_2O_2 molar ratio was increased to 1:2 and 1:3, there was no significant change in benzylamine oxidation (entry 5). Hence, 1:2 molar ratio of benzylamine: H_2O_2 , 2 mmol of the benzylamine, 80 mg of [VO(PS-BBMA]SO₄ for 10 h at 80 °C was the most optimized condition for the benzylamine oxidation (entry 2).

Under optimized reaction conditions, unsupported [VO(BBMA]SO₄ complex and VOSO₄ salt were tested for benzylamine oxidation. It was observed that [VO(BBMA]SO₄ showed 32 % yield of benzamide with 100 % selectivity whereas VOSO₄ gave 25 % yield.

Table 3

| Entry | Temperature | Benzylamine: | Oxidants | Catalyst | Yield ^a |
|-------|-------------|--------------|----------|--------------------|--------------------|
| | (°C) | H_2O_2 | | concentration (mg) | (%) |
| 1 | 70 | 1:2 | H_2O_2 | 80 | 90 |
| 2 | 80 | 1:2 | H_2O_2 | 80 | 92 |
| 3 | 90 | 1:2 | H_2O_2 | 80 | 85 |
| 4 | 80 | 1:1 | H_2O_2 | 80 | 51 |
| 5 | 80 | 1:3 | H_2O_2 | 80 | 92 |
| 6 | 80 | 1:2 | H_2O_2 | 70 | 72 |
| 7 | 80 | 1:2 | H_2O_2 | 90 | 92 |
| 8 | 80 | 1:2 | TBHP | 80 | 63 |
| 9 | 80 | 1:2 | O_2 | 80 | 42 |
| 10 | 80 | 1:2 | H_2O_2 | Blank reaction | 15 |

Optimization of the reaction conditions

a Isolated yield.

Similarly, blank reaction without catalyst gave only 15 % of product (Table 3, entry 10). By keeping these optimized reaction conditions, various electronically and structurally diverse benzylamines were subjected to oxidation at optimized reaction conditions and the results from these studies are shown in Table 4. The results indicated that both electron rich and electron deficient benzylamines could be successfully transformed into their corresponding products in moderate to good yields. Specifically, excellent yields were obtained for 4-methyl-substituted benzylamine (Table 4, entry 2) and 4-methoxy-substituted benzylamine (Table 4, entry 10). On the other hand, strong electron-withdrawing groups such as Cl and NO₂ induced lower reaction efficiency. The meta substituted group on the benzylamine gave lower yields (entries 3, 5, and 8) as compared to para substituted benzyl amines.

Table 4

Substrate scope of benzylamine surrogates

| Entry | Benzylamines | Benzamides | Yield ^b |
|-------|--------------|------------|--------------------|
| | | | |





General conditions: Substituted benzylamines (2 mmol), H_2O_2 (2 mmol), VO(PS-BBMA)(H_2O)(SO₄) (80 mg, 0.08 mmol), 80 °C, 10 h. b Isolated yields.

3.3. ¹H-NMR spectral data of amides

1. Benzamide

¹**H NMR** (**400 MHz, CDCl**₃): δ 7.75-7.74 (m, 2H), 7.49-7.19 (m, 3H), 6.00 (bs, 1H), 5.60 (bs, 1H).

2. 4-methylbenzamide

¹H NMR (400 MHz, CDCl₃): δ 7.72-7.70 (m, 2H), 7.26-7.24 (m, 3H), 6.02 (bs, 1H), 5.65 (bs,

1H), 2.41 (s, 3H).

3. 3-methylbenzamide

¹**H NMR (400 MHz, CDCl₃)**: δ 7.65-7.57 (m, 1H), 7.34 (m, 1H), 7.33-7.26 (m, 2H), 6.07 (bs, 1H), 5.68 (bs, 1H), 2.41 (s, 3H).

4. 4-nitrobenzamide

¹H NMR (400 MHz, CDCl₃): δ 8.31-8.29 (m, 3H), 8.10-8.08 (m, 2H), 7.73 (bs, 1H).

5. 3-nitrobenzamide

¹**H NMR** (**400 MHz, CDCl**₃): δ 8.70-8.39 (m, 1H), 8.37-8.30 (m, 3H), 7.79-7.73 (m, 2H).

6. nicotinamide

¹**H NMR (400 MHz, DMSO**): δ 9.03-8.76 (m, 1H), 8.75 (m, 1H), 8.19-8.16 (m, 1H), 7.44-7.27 (m, 1H), 6.29 (bs, 1H), 6.01 (bs, 1H).

7. 4-chlorobenzamide

¹**H NMR** (**400 MHz, CDCl₃**): δ 7.69-7.67 (m, 2H), 7.37-7.19 (m, 2H), 5.94-5.89 (bs, 2H).

8. 3-chlorobenzamide

¹**H NMR (400 MHz, DMSO**): δ 7.82-7.67 (m, 1H), 7.52-7.50 (m, 1H), 7.41 (m, 1H), 7.26 (m, 1H), 6.07-5.90 (2 bs, 2H).

9. N-phenylbenzamide

¹H NMR (500 MHz, CDCl₃): δ 7.84-7.79 (m, 5H), 7.52-7.25 (m, 5H), 6.50 (bs, 1H).

10. 4-methoxybenzamide

¹**H NMR** (**400 MHz, CDCl**₃): δ 7.74-7.72 (m, 2H), 7.24-7.22 (m, 2H), 5.92 (m, 2H), 3.73 (s, 3H).

Recycling ability

One of the main objectives of supporting a metal complex on a polymer is to enhance the lifetime of the resulting catalyst. To verify this property in the current systems, the catalyst [VO(PS-BBMA]SO₄ was separated from the reaction mixture after each run by filtration, washed with alcohol and dried before using it in subsequent runs. The catalyst could be recycled up to seven times (Fig. S11) without much loss in its activity. In order to see whether the present catalyst was functioning in a truly heterogeneous manner, the conventional hot filtration test was carried out for all the oxidation reactions under the optimized conditions. After 1 h, the catalyst was immediately filtered off from the hot reaction mixture in order to avoid re-adsorption of any leached metal onto the catalyst surface. The filtrate was collected and the reaction was continued for another 2 h, showed no further increase in conversion. Vanadium content in the hot filtrate and recycled catalyst was determined by ICP-OES and the absence of vanadium indicated that the reaction was truly heterogeneous in nature. % of metal present in the catalyst after performing the reaction was determined (Fig. S12). It was found that up to fifth cycle the metal remains same and after that there was slight decease in metal content.

4. Conclusion

Polymer immobilized vanadium complex [VO(PS-BBMA]SO₄ has been synthesized and characterized by physicochemical techniques. The catalytic activity of [VO(PS-BBMA]SO₄ has been examined for liquid phase oxidation of benzylamine to benzamide using H_2O_2 as oxidant. Under optimum reaction conditions, catalyst showed highest benzylamine conversion (92 %) and 100 % selectivity for benzamide. Various benzamide surrogates have been synthesized in moderate to good yields under mild and neutral reaction conditions. So this study reveals that catalyst can be a convenient ecofriendly substitute for hazardous stoichiometric oxidants without solvent. This catalyst can be used in oxidation of benzylamine up to seven cycles without any loss in activity.

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Authors declare 'no conflict of interest'.

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GRAPHICAL ABSTRACT



Highlights

- Novel unsupported and polymer supported complexes were prepared and characterized
- Geometry of the complexes were confirmed by CHN, ESR, IR, Electronic and LC-M spectrum
- Elegant method for the preparation of amides using H_2O_2 in solvent free conditions
- The developed catalyst was facilely recovered, truly heterogeneous and reusable



Figure 1



Figure 2