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Renewable waste rice husk grafted oxo-vanadium catalyst for oxidation of tertiary amines to N-oxides

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Low cost renewable waste rice husk (RH) has been used as a support for grafting of oxo-vanadium Schiff base via covalent attachment for the oxidation of tertiary amines to N-oxide. The synthesis of desired RH grafted oxo-vanadium complex involves the prior functionalization of RH support with amino-propyltrimethoxysilane (APTMS) followed by its reaction with salicylaldehyde to get RH-functionalized Schiff base which subsequently reacted with vanadyl sulphate to get the targeted oxo-vanadium catalyst. The synthesized catalyst was found to be efficient heterogeneous catalyst and afforded excellent yield of corresponding N-oxides via oxidation of tertiary amines with hydrogen peroxide as oxidant. Furthermore, the synthesized catalyst was found to be quite stable and showed consistent activity for five runs without any loss in activity

Introduction

Owing to the increasing environmental consciousness, there is a pressing need to develop methodologies for the effective utilization of biomass waste as it not only creates disposal problems but also causes environmental pollution¹⁻⁸. Rice husk (RH) is one of such a major by-product of the rice-milling industries and is produced abundantly every year throughout globe. RH contains 25-35% cellulose, 8-21% the hemicelluloses, 26-31% lignin, 15-17% amorphous silica and waxes, and 2-5% of other soluble substances⁹⁻¹². Moreover, after it's burning approximately 20% ash content comprises over 95% of amorphous silica which has very fine particle size, very high purity, high surface area, and high porosity^{13-14.} These properties make the utilization of RH in various areas including catalysis, a very economically attractive perspective. In this context, Adam et al. reported the use of RH silica as support matrix for the grafting of various types of transition metals and their catalytic potentials in the oxidation, acylation and benzylation reactions¹⁵⁻¹⁷.

Oxidation of tertiary amines to N-oxides is an important transformation as these compounds have found extensive applications as precursors in the synthesis of bioactive molecules, offer structural modification and functional group manipulation possibilities[¹⁸]. Apart from the conventional oxidants such as activated $H_2O_2^{19}$, a-azo hydroperoxides²⁰, Caro's acid $(H_2SO_5)^{21}$, dioxirane²² and peracids²³, which generate large amounts of undesirable waste, a number of metal catalysts such as methyltrioxorhenium²⁴, manganese porphyrin²⁵, flavin²⁶, TS-1²⁷, tungstate-exchanged Mg/Al-

layered double hydroxide acid²⁸, tungsten sulphide²⁹, polyperoxometalates³⁰, selenium³¹ tungsten-based and molybdenum oxides³² have been shown to catalyze the Noxidation of tertiary amines in the presence of aqueous H_2O_2 . However, these reported methods suffer from certain drawbacks such as homogeneous nature, multi-step synthetic procedures, high cost and non-renewable support matrices. To the best of our knowledge, heterogenized metal catalyst using renewable supports has never been realized for this transformation.

Herein we report the successful synthesis of rice husk (RH) grafted oxo-vanadium Schiff base through covalent linkage and its application for the oxidation of tertiary amines to N-oxides using hydrogen peroxide as green oxidant (Scheme 1). This is a simple and clean methodology where compounds formed are free from any contaminating by-products and the catalyst shows good activity as well as facile recovery by simple filtration for recycling runs.



Scheme 1: RH-grafted oxo-vanadium Schiff base catalyzed oxidation of tertiary amines

3. Results and discussions

3.1 Synthesis and characterization of catalyst

The schematic representation of the synthesis of RH-grafted oxo-vanadium Schiff base is shown in Scheme 2. The preparation of RH-grafted oxo-vanadium Schiff base catalyst and intermediate steps was examined and monitored using

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various techniques XRD, FTIR, TGA, and scanning electron microscopy (SEM).



Fig. 1 shows the XRD pattern of bare RH and RH-grafted oxovanadium Schiff base. As shown in Fig. 1a, RH did not show any sharp diffraction pattern, which indicates that the sample is amorphous in nature.³³ A broad diffraction peak observed at 25° is attributed to the amorphous silica. The XRD pattern for RH-grafted oxo-vanadium Schiff base revealed some sharpness in the peak which is due to the presence of vanadium which indicates the semi crystalline nature of the synthesised material as shown in fig. 1b.



Surface morphologies of the synthesized materials were determined by scanning electron microscopy (Fig. 2). Figure 2*a* shows the SEM image of virgin rice husk particles, where the structure resembles to an irregular and highly porous siliceous structure, which is in well agreement with the other literature reports.³⁴ Figure 2b shows the SEM image of RH-grafted Schiff base. Significant change in the morphology is observed with the presence of a large number of button- like structures or

bumps interspaced with small pores which are absent on the virgin rice. These buttons like structures or bumps may be attributed to the obstruction of silica fibre to devolatilization. Figure 2c shows the SEM image of RH-grafted oxo-vanadium Schiff base with only difference in the appearance of small white dots which may be probably due to the presence of vanadium metal in the synthesized material. Further Figure 2d, e, and f show the EDX of neat RH, RH-Schiff base and RHgrafted oxo-vanadium Schiff base respectively. A typical composition of the rice husk contains various minerals such as Fe_2O_3 , MgO, K_2O , Al_2O_3 etc in 0.5 to 2 wt%.³⁵ The EDX of Rice husk (RH) shows only C, O and N (Fig. 2d) as the area for SEM micrographs was randomly selected where the EDX analysis was done. However, in other two Figures (2e-f) appearance of other elements such as Si, Al, K etc confirmed the presence of various minerals in the rice husk. The presence of vanadium in the final catalyst (Fig. 2f), confirmed the successful synthesis of the desired material.



Fig. 2 : SEM images and EDX of a,d) Neat RH; b,e) RH-grafted Schiff base; c,f) RH-grafted oxo-vanadium Schiff base.

The chemical changes occurred during the immobilization of oxo-vanadium Schiff base on RH was monitored by FTIR.³⁶⁻³⁷ Figure 3 shows vibrational assessments of RH, RH-NH₂, RHgrafted Schiff base and RH-grafted oxo-vanadium Schiff base. The presence of an intense and broad peak in the range 3000-3700 cm⁻¹ in virgin RH attributed to the stretching mode of hydrogen bonded Si-OH groups. Other vibrational streching modes observed at 2915 cm⁻¹ and 2847 cm⁻¹ are due to the presence of lignin in rice husk containing methyl and methylene groups. In Fig. 3a, the peaks at 1725 and 1100 cm⁻¹ are related to the aldehydic and the Si-O-Si groups, respectively in rice husk. The bands between 800 cm⁻¹ and 540 cm⁻¹ suggested the presence of Si-H bonds and deformation of Si-O bonds. In Figure 3a,b, the band at 1639-1640 cm⁻¹ is attributed to the presence of water molecules bound to the silica matrix as well as ketonic groups presented in the hemicellulose of rice husk. In case of Schiff base grafted RH (Fig. 3c), the peak at 1646 cm⁻¹ is found to be more intense due to the additional stretching of C=N groups formed due to the condensation of -NH₂ with carbonyl groups. After the reaction of Schiff base-RH with vanadyl sulphate in figure 3d, the band has been shifted to higher wavelength 1652 cm⁻¹ due to the interaction with metal ions. In addition the appearance of

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characteristic peak at 613 cm^{-1} due to V=O, confirmed the succesful synthesis of the desired material (Fig. 3d).



Fig. 3: FTIR Spectra of a) RH b) RH-NH $_2$ c) RH-grafted Schiff base; d) RH-grafted oxo vanadium Schiff base Catalytic activity

Thermal degradation and corresponding weight loss in RH, RHgrafted Schiff base and RH-grafted oxo-vanadium Schiff base was determined by thermogravimetric analysis (TGA) and differential thermal analyses (DTA) as shown in Figure 4. In case of RH, initial weight loss below100 °C can be assigned due to the decomposition of adsorbed water molecules. The major weight loss in the range of 200-300 °C is mainly due to the decomposition of other organic moieties³⁸. Further, in case of RH-grafted Schiff base major weight loss in the range of 300-400 °C can be attributed to the decomposition of Schiff base moieties presented on the RH surface. Fig. 4c shows the TGA-DTA curves for the RH-grafted oxo-vanadium Schiff base having first small weight loss below 100 °C is due to decomposition of water molecules and other major weight loss in the range 250-400 °C is due to the decomposition of Schiff base and other moieties of RH.



Fig. 4: TG-DTA curves for a) neat RH b) RH-grafted Schiff base; c) RH-grafted oxovanadium Schiff base

Catalytic activity

The catalytic activity of the prepared RH-grafted oxo-vanadium Schiff base and its comparison with homogenous analogue was studied for oxidation of tertiary amines to corresponding Noxides using hydrogen peroxide (30 wt% aq.) as oxidant (Scheme 1). Oxidation of triethylamine was selected as a model substrate to optimise the reaction conditions by varying the reaction parameters such as solvent, temperature and catalyst amount (Table 1). In the absence of any solvent under neat condition, the reaction was found to be very slow and only trace amount of the product was obtained even after prolonged reaction time (Table 1, entry 1). However, among the various solvents such as water, acetonitrile, methanol, THF and dichloroethane (Table 1, entry 2-7) studied, acetonitrile was found to be best solvent and afforded highest product yield within 4h. The reaction was found to be very slow at room temperature; whereas 80 °C was found to be optimum and afforded maximum product yield within 6h (Table 1, entry 8). Furthermore, no reaction occurred in the absence of catalyst under described reaction conditions (Table 1, entry 9). Further, to compare the catalytic efficiency of RH-grafted heterogeneous catalyst with its corresponding homogeneous analogue, we synthesized oxo-vanadium Schiff base from 2hydroxybenzaldehyde and ethylenediamine by following the literature procedure.³⁹ Thus obtained Schiff base was treated with vanadyl sulphate hydrate (VOSO₄.xH₂O) in 1:1 molar ratio to get homogeneous oxo-vanadium Schiff base.⁴⁰ The synthesized homogeneous oxo-vanadium Schiff base was tested under optimized reaction conditions i.e catalyst amount 0.002 mmol, acetonitrile at 80 °C. After the 12h reaction time, the yield of the product was found to be 93% (Table 1, entry 9).

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| Table 1: Results of the optimization experiments ^a | | | | | | |
|---|----------|----------------|---------------|-------------|----------------------------------|----------------------------------|
| Entry | Solvent | oxidant | Temp. (°C) | Time (h) | Conv. (%) | Yield (%) ^b |
| 1 | - | H_2O_2 | 80 | 24 | trace | - |
| 2 | Methanol | H_2O_2 | 65 | 6 | 80 | 80 |
| 3 | Water | H_2O_2 | 100 | 12 | 50 | 45 |
| 4 | DCM | H_2O_2 | 40 | 10 | 85 | 82 |
| 5 | tBuOH | H_2O_2 | 86 | 7 | 70 | 68 |
| 6 | THF | H_2O_2 | 66 | 12 | 60 | 55 |
| 7 | Toulene | H_2O_2 | 110 | 20 | 30 | 25 |
| 8 | CH₃CN | H_2O_2 | - | 6 | 15 [°] , | Trace |
| | | | | | 78 ^d ,94 ^e | 72 ^d ,92 ^e |
| 9 | CH₃CN | H_2O_2 | 80 | 12 | - ^f ,95 ^g | - ^f ,93 ^g |
| 10 | CH₃CN | твнр | 80 | 10 | 60 | 55 |
| | | O ₂ | | | 40 | 38 |
| | | | | | | |

^aReaction conditions: triethylamine (2.0 mmol), catalyst (0.1 g, 0.002 mmol), solvent (4 mL) in the presence of $H_2O_2(3.0 \text{ mmol})$; ^bIsolated yield; at ^c25 °C, ^d60 °C; ^e80 °C; ^fIn the absence of catalyst; ^gusing Homogeneous oxovanadium Schiff base (amount 0.002 mmol, temp. 80 °C, CH₃CN solvent in 12 h gave 93 % yield).

The RH-grafted oxo-vanadium Schiff base was found to be equally efficient as homogeneous analogue. However, the facile recovery and efficient recycling of the heterogeneous catalyst make the developed catalyst more effective and desirable from both environmental and economical viewpoints. Similarly, the use of aq. TBHP and molecular oxygen as oxidant in place of hydrogen peroxide afforded poor product yields (Table 1, entry 10).

Thus, the optimized reaction conditions for the present reaction comprises the oxidation of triethylamine (2 mmol) with hydrogen peroxide (3 mmol) in the presence of RHgrafted oxo-vanadium Schiff base (0.1g,) in acetonitrile (4 ml) under refluxing conditions. After completion of the reaction as analyzed by TLC (SiO₂), the catalyst was easily separated by simple filtration and reused as such for subsequent runs. The filtrate was subjected to the usual workup to extract the corresponding N-oxide. Further, the reaction was extended to a variety of tertiary amines including aromatic, heterocyclic and aliphatic under the described reaction conditions. The results of these experiments are summarized in Table 2. Among the various substrates, amines having aliphatic substituents were found to be more reactive (Table 2, entry 1-3) than substituted pyridines (Table 2, entry 4-10). Among the various pyridines, those substituted with electron donating groups were found to be more reactive (Table 2, entry 4-7). Aliphatic amines such as triethylamine, N-methylmorpholine and triethanolamine also reacted well and afforded moderate to high product yield (Table 2, entry 11-13). Strically hindered tertiary amine such as N,N-dimethylbenzylamine also afforded reasonably good yield of the corresponding product under

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described reaction conditions (Table 2, entry 14). However, in case of N,N-dimethylaminopyridine under described reaction conditions, selective formation of N,N-dimethylaminopyridine N-oxide obtained without any evidence for the formation of any by-product which could be obtained due to the oxidation of nitrogen of N,N-dimethylamino group or both. This is in well agreement with the existing report.⁴¹

Table 2: RH-grafted oxo-vanadium Schiff base catalyzed oxidation of tertiary amines^a Yield^[b] Entry Substrate Product (%) v́≁o 1 92 -0 90 2 C₂H₅ C_2H_5 N(≁O 85.84.86. 3. R=CH₃,Cl, Br, OCH₃ 88 R=CH₃,CI, Br, OCH₃ 65 4. 72 70

7. N CH₃





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^aReaction conditions: substrate (2.0 mmol), catalyst (0.1 g), acetonitrile (4 ml) in the presence of H_2O_2 (3.0 mmol) at 80 °C for 4h; ^bIsolated yield; ^c 6.0 mmol of H_2O_2 is used.

Further, we checked the recycling of the recovered RH-grafted oxo-vanadium Schiff base catalyst for oxidation of triethylamine as representative substrate. After completion of the reaction the catalyst could easily be recovered by filtration, dried and used for subsequent runs. The recyclability of the catalyst was checked for five runs. In all experiments the reaction time and yield of desired product remained almost similar as shown in Fig 5, establishing the efficient recycling of the catalyst. Furthermore, to ascertain the leach-proof nature of the catalyst following reaction was performed: a reaction mixture containing catalyst and oxidant was refluxed for three hours. After being cooled at room temperature, the catalyst was recovered by filtration and the filtrate was charged with fresh substrate and oxidant and stirred the mixture under reflux for three hours. The oxidation did not take place, indicating that there was no leaching during the reaction and the reaction was truly heterogeneous. This was further supported by ICP-AES analysis of recovered catalyst, where percentage of the vanadium in recovered remained almost similar to fresh one 1.19 wt%.



2. Experimental section

2.1 Materials

All reagents and solvents were obtained from commercial sources and used without further purification. Rice Husk (RH) was obtained from sangam rice mill, mehal kalan in Punjab, India. Aminopropyltrimethoxysilane (>97 %), Vanadyl sulfate and salisaldehyde (>98 %) were purchased from Sigma-Aldrich and used without further purification. Hydrogen peroxide (30 wt%), and other solvents were of analytical grade and were used as received. Distilled water was used throughout the synthesis.

2.2 Techniques used

Rice husk is powered on RETSCH Planetary Ball Mill PM 100. FT-IR spectra were collected on a Nicolet 8700 FT-IR spectrometer in the region of 4000-400 cm⁻¹. SEM images were obtained on a FEI Quanta 200 F using tungsten filament doped with lanthanum hexaboride (LaB₆) as an X-ray source, fitted with an ETD (Everhart Thornley Detector), which preferentially work as a secondary electron detector. The sample for SEM was prepared by dispersing the sample on an adhesive coated carbon paper followed by gold coating. XRD analysis were carried out on Bruker D8 Advance diffractometer at 40 kV and 40 mA with Cu K_{α} radiation (λ = 0.15418 nm) in the range 2°-80°. The thermo gravimetric analysis (TGA) was done using a thermal analyzer TA-SDT Q-600. ICP-AES analysis was carried out by inductively coupled plasma atomic emission spectrometer (ICP-AES, DRE, PS-3000UV, Leeman Labs Inc., USA). Samples for ICP-AES were prepared by leaching out 0.01 g of sample with HNO_3 (conc.), and then heated for 30 min and volume to 10 mL.¹H-NMR and ¹³C NMR spectra of the products were recorded at 500 MHz by using Bruker Avance-III 500 MHz instrument. GCMS was carried out by using HP 5972 MSD couple with HP 5890 GC, HP (USA) 1998.

2.3 Synthesis of amino functionalized rice husk (RH-NH₂)

Firstly the rice husk obtained is washed with water and ethanol and then dried in an oven overnight and then powdered it in a ball mill. In a typical synthesis, 2.0 g of RH was adequately dispersed in 50 mL toluene by using an ultrasonic probe. Subsequently, 6.0 mL of APTMS was added to the RH dispersion and then the reaction vessel was refluxed for 24 h under a nitrogen atmosphere. After completion of the reaction, the amino functionalized RH (RH-NH₂) was washed with toluene to remove excess/non-reacted APTMS followed by its drying at 70 $^{\circ}$ C under vacuum.

2.4 Synthesis of RH-grafted oxo-vanadium Schiff base

Briefly 1.0 g of amino functionalized RH was dispersed in 50 ml ethanol using an ultrasonic bath. This is followed by addition of 3mL of salicylaldehyde. The reaction mixture was refluxed for 8 h under a nitrogen atmosphere in order to execute the reaction between amino groups of APTMS moieties and salicylaldehyde. After completion of the reaction, four consecutive ethanol washings were performed to remove the non-reacted salicylaldehyde and the obtained yellow coloured material was dried in an oven at 70 $^\circ\text{C}$ overnight. Further in the final step, 1 g of Schiff base immobilized Rice Husk was dispersed in methanol and refluxed for 24 h in the presence of 0.5 g vanadium sulphate hydrate (VOSO₄.xH₂O) under a nitrogen atmosphere to obtain the desired RH-grafted oxovanadium Schiff base as shown in Scheme 2. The obtained material was thoroughly washed with methanol to remove the undigested vanadium sulphate. Washing of the final product was repeated 3-4 times and then it dried in an oven. This greenish powder, RHgrafted oxo-vanadium Schiff base, was used as a catalyst for the oxidation of tertiary amines to N-oxides. Further the loading of vanadium in the prepared catalyst was found to be 1.2 wt% as determined by ICP-AES analysis.

2.5 General experimental procedure

Into a stirred mixture of tertiary amine (2.0 mmol) and catalyst (0.1 g, 0.002 mol) in acetonitrile was added aqueous 30 wt % H_2O_2 (3.0

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mmol) and the resulting mixture was stirred at 80 $^{\circ}$ C for 4h. The progress of the reaction was monitored by TLC (SiO₂). At the end of the reaction, the catalyst was removed by filtration and reused for subsequent recycling runs. The filtrate was concentrated under reduced pressure. The residue thus obtained was purified by column chromatography (SiO₂, hexane/ethyl acetate, 6:4). The yields of the N-oxide and their reaction times are presented in Table 2. The conversion of the reaction product was determined by GC analysis. The identity of the products was established by comparing with their physical and spectral data with those of authentic samples.^{42,43}

Conclusion

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The present work shows a unique application of bio waste rice husk as a support material for development of heterogeneous catalyst for organic transformation by considering the rich -OH functionalities of the RH support. The APTMS grafted RH support was prepared by chemical interaction between amino groups of APTMS and oxygen functionalities available on the RH support. Subsequent reaction with salicylaldehyde to give RH-grafted Schiff base which further reacted with vanadyl sulphate to give corresponding RH-grafted oxo-vanadium Schiff base through covalent attachment. The successful synthesis of the desired catalyst was confirmed by thorough characterization of the catalyst by various techniques such as XRD, FTIR, SEM-EDX, TGA and ICP-AES analysis. The developed catalyst was utilized as a heterogeneous catalyst for the oxidation of tertiary amines to N-oxides using hydrogen peroxide as an oxidant. Moreover, the developed catalyst was found to be easily recoverable and recyclable without significant loss in the catalytic activity. This work with added benefits of flexibility in immobilization of various chemical moieties and on bio-waste rice husk offers new opportunities for designing highly active heterogeneous catalysts for organic transformations.

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