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A Novel Vanadium n-propylamino Phosphate Catalyst: Synthesis, Characterization and Applications

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A novel, lamellar type Vanadium n-propylamino phosphate catalyst is synthesized and characterized by using various physicochemical techniques such as Powder X-ray diffraction, Scanning electron microscopy/Energy dispersive X-ray analysis, Thermogravimetry/Differential thermal analysis, Fourier transform Infrared analysis, Electron spin resonance spectroscopy, Ultraviolet – Visible Diffuse reflectance spectroscopy, X-ray Photoelectron spectroscopy, ^{31}P Magic angle spinning Nuclear Magnetic Resonance spectroscopy and Catalytic applications toward Octahydroquinazolinone synthesis. It is found that the n-propylamine is present as sandwich between Vanadyl phosphate layers. Most of the Vanadium is present as V^{4+} ions in tetrahedral co-ordination. Vanadium n-propylamino phosphate catalyses Octahydroquinazolinone synthesis more effeciently and the optimum conditions required for Octahydroquinazolinone synthesis are, Benzaldehyde (2 mmol), Dimedone (2 mmol), Urea (4 mmol), Methanol + Water (1:1, 5 mL) and Catalyst (0.05 g). A plausible mechanism is also proposed.

Keywords: *vanadium, n-propylamino phosphate, octahydroquinazolinones, synthesis*

1. Introduction

The Octahydroquinazolinones derivatives have attracted considerable attention, as they exhibit potent antibacterial activity against Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa[1], and calcium antagonist activity[2,3]. In 1893, Italian chemist Pietro Biginelli was first reported, the acid catalyzed cyclocondensation reaction of an aldehyde, ethylacetoacetate and urea. This procedure known as Biginelli reaction. Recently, the Biginelli reaction has been found to employ in the synthesis of Octahydroquinazolinones, which involves Knoevenagel condensation, Michael addition and cyclization of aromatic aldehydes, urea and cyclic β-diketones[4]. Various Lewis acid catalysts such as Mn $(OAc)_3$, LiBr, VCl_3, La $(OTf)_3$, $ZrCl_4$, and $InBr_3$, are employed in the synthesis of dihydropyrimidinones through Biginelli reaction. However the reagents/catalysts are found to be expensive, harmful and are difficult to handle especially in large scale. Literature survey reveals a number of homogeneous and heterogeneous catalytic systems used for synthesis of octahydroquinazolinone derivatives which includes TMSCl[5], conc. H_2SO_4, Nafion-H[6], $VOSO_4$, conc. HCl in ethanol[7], ammonium metavanadate[8], ionic liquids[9] and silica sulfuric acid[10]. However the procedures are having several drawbacks.

Vanadium containing micro porous molecular sieves was found to be active in a number of oxidation reactions. They are industrially important in a number of catalytic processes such as the selective oxidation of hydrocarbons, production of SO_3, ammoxidation of hydrocarbons and reduction of nitric oxide[11]. Vanadium phosphates (VPO) are having many applications in catalysis, materials science and as heterogeneous catalysts in various organic reactions, because of the nontoxic nature and the ability to promote selective reactions. VPO constitute a interesting class of layered compounds exist in a wide range of structural forms due to the variable valency of Vanadium as well as the large diversity in VO_6 octahedron bonding and PO_4 structural units. Phases containing Vanadium in +5, +4 and +3 oxidation states and co-ordination geometry (tetrahedral, square pyramidal and octahedral) are known. In all the compounds the layers are held together by hydrogen bonding or by weak Vander Waal's interactions and the layered compounds are amenable for intercalation reactions. VPO catalysts are extremely important in heterogeneous catalysis for the selective oxidations of methanol to formaldehyde[12], benzyl alcohol to benzaldehyde[13], esterification of oleic acid[14], Ammoximation of aromatics and alkyl aromatics[15], n-butane to maleic anhydride[16], propane to acrylic acid[17], oxidative dehydrogenation of ethane and propane[18], epoxidations of allylic alcohols[19].

The concept of using micelles and long chain surfactants as templates for the synthesis of novel mesoporous silicates was first introduced by a group of scientists at Mobil in 1992[20]. From the literature studies, the neutral templating approach using amines as templates leads to the formation of lamellar VPO phases[21]. The role of organic structure directing agents has been discussed[22] as an important role in the kinetics of nucleation and crystallization. The development of Vanadium containing materials with novel structures and well defined oxidation states of Vanadium is an important area of research in oxidation catalysts. Reports are available regarding the applications of Vanadium as a

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catalyst in organic synthesis such as synthesis of coumarins[23], 3, 4-dihydropyrimidin-2(1H)-ones, bis-(indolyl) methane's[24], trimethylsilylation of alcohols[25], tris (2, 4-dinitrophenoxo) compounds[26] and mannich-type reactions[27].

Recently, Venkatathri et al.[28], reported a novel Manganese organophosphate and Titanium n-propylamino phosphate synthesized using amines as templates. The aim of the present study is to synthesis Vanadium n-propylamino phosphate and characterize it by various physico-chemical techniques such as, powder XRD, SEM/EDAX, TG/DTA, FT-IR, ESR, UV-Vis DRS, XPS and ^{31}P MAS NMR. We are also used the above catalyst for the synthesis of Octahydroquinazolinone derivatives and studied the influence of various synthesis parameters.

2. Experimental

2.1. *Materials*

Vanadyl sulphate (98%, Loba Chemie, India), n-propyl amine (Spectrochem, India), Orthophosphoric acid (85%, Merck, India), aldehydes (Sisco, India) and dimedone (Oakwood, USA) were used without further purification.

2.2. *Synthesis*

A calculated quantity of 0.01 molar Vanadyl sulphate, was added to 1 molar orthophosphoric acid and stirred mechanically for 5-10 minutes to form a homogeneous mixture. To the well stirred mixture, a 4 molar n-propylamine was added and stirred well to get solid homogeneous Vanadium n-propylamino phosphate. The catalyst was ground well, washed with ether and dried at 40 °C for 5-10 minutes. The resulting solid was subjected to various physico-chemical characterizations.

The Vanadium n-propylamino phosphate catalyst was analyzed by powder X-ray diffraction using a spectrometer (Philips X'pert Pro PW-3040 model, special detector – X'elerator) supported by small and wide angle goniometers with voltage and current of 40 kV and 30 mA respectively at room temperature in a 2θ range of 0 to 50°. The morphology and surface elemental composition of the catalyst were investigated by using scanning electron microscope with EDAX attachment on a JEOL-JSM-5200 electron microscope. The thermal characteristics of the Vanadium n-propylamino phosphate has been studied by Thermo gravimetry/Differential thermal analysis (Diamond TG/DTA thermal analyzer) in a temperature range from 25 to 900 °C with heating rate of 10 °C/min in Nitrogen atmosphere. Fourier transform Infrared spectrum was recorded on a Shimadzu spectrophotometer using KBr pellet technique. Electron spin resonance spectrum was obtained from Bruker instrument. The co-ordination and oxidation state of Vanadium in Vanadium n-propylamino phosphate was examined by using diffuse reflectance UV–visible spectrometer (Shimadzu UV 2550) with 200 to 800 nm region and Barium sulphate was used as reference. X-ray photoelectron spectroscopy of Vanadium n-propylamino phosphate was obtained from ESCA-3000. ^{31}P Magic angle spinning nuclear magnetic resonance spectrum were obtained from Bruker MSL-300 instrument.

In a typical reaction, benzaldehyde (2 mmol), dimedone (2 mmol) and urea (4 mmol) were taken in a round bottomed flask. To the above reaction mixture 0.05 g Vanadium n-propylamino phosphate catalyst was added. The reaction mixture was kept under stirring and reaction progress was monitored by TLC. The solid product was filtered and recrystallized with ethanol. The products were authenticated by melting point, FT-IR and ^{1}H NMR.

3. Results and Discussions

The powder X-ray diffraction pattern (Figure 1) of Vanadium n-propylamino phosphate shows peaks at 7.02°, 8.7°, 13.1°, 13.8°, 17.4°, 19.0°, 21.1°, 22.4°, 24.3°, 25.2°, 26.2° and 32.1°, 2θ values and the corresponding d-spacing's are 12.5 Å,

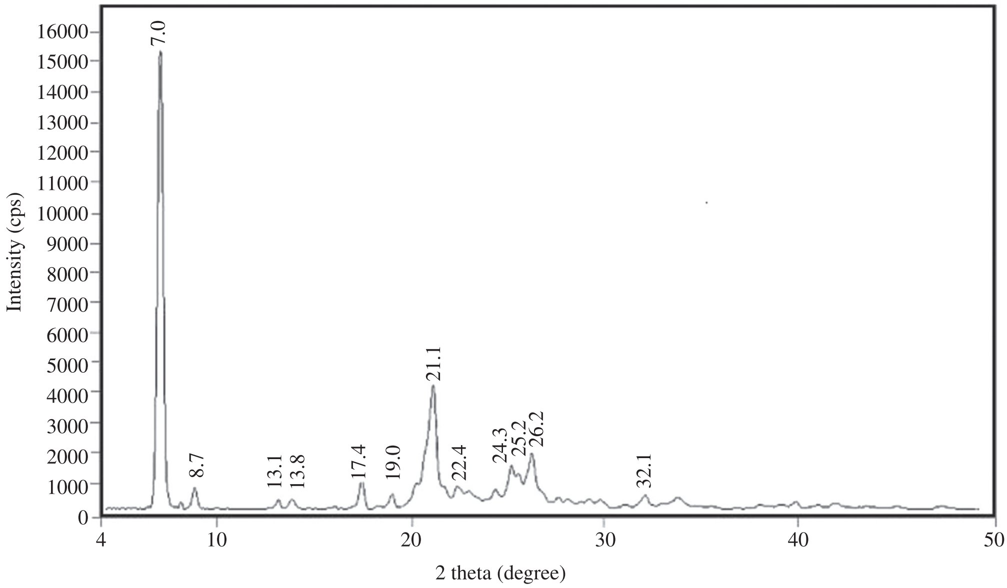


Figure 1. Powder X-ray diffraction pattern of Vanadium n-propylamino phosphate.

10.0 Å, 6.7 Å, 6.3 Å, 5.08 Å, 4.6 Å, 4.2 Å, 3.9 Å, 3.6 Å, 3.5 Å, 3.3 Å, and 2.7 Å. The peaks at 21.1° and 26.2° values indicates the presence of Vanadium ions[29] predominantly in V^{4+} state with small amount in V^{5+}[30] and peak at 19.0° indicates the presence of Vanadium phosphate[31] layer. The peaks at 13.9°, 19°, 22°, 24° and 26.2° are due to the presence of $VOPO_4$ phases[32] in Vanadium n-propylamino phosphate.

The Scanning electron micrograph (Figure 2) shows homogeneous distribution of the material with plate like structures[33] and 15-30 µm particle size. The Energy dispersive X-ray analysis (Figure 3) shows the presence of Vanadium ions on surface.

The Thermogravimetry/Differential thermal analysis (Figure 4) of Vanadium n-propylamino phosphate shows endothermic weight loss at 100-150 °C are due to volatilization of physically adsorbed water molecules[34]. The exothermic weight loss at 230-500 °C is due to the oxidative decomposition of organic molecules[35].

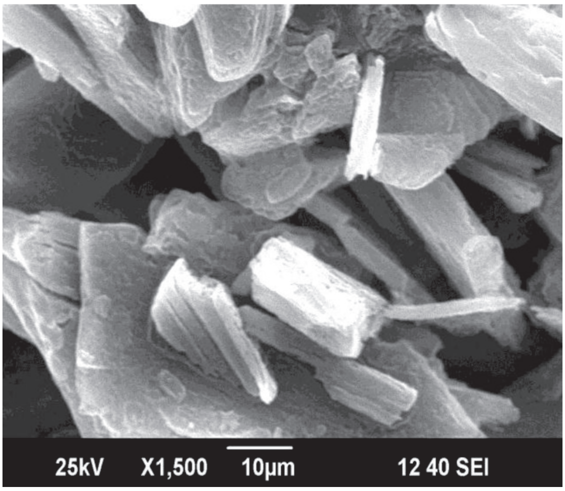


Figure 2. Scanning electron micrograph of Vanadium n-propylamino phosphate.

The Fourier transform Infrared spectrum (Figure 5) of Vanadium n-propylamino phosphate shows a peak at 534 cm^{-1} associated with the V-O-V rotational vibrations[29]. Peak at 1468 cm^{-1} is due to the presence of hydrocarbon moiety ($-CH_2-CH_2-$)[36]. While the peak at 756 cm^{-1} was due to asymmetric stretching vibrations of V-O-V units[37]. A peak around 1220-1080 cm^{-1} corresponds to C-N stretching vibration[38]. Peak at 1396 cm^{-1} may be due to P-O stretching vibration[39]. Peak at 970 cm^{-1} is due to stretching vibration of V=O in the infrared spectrum[40]. The band at 436 cm^{-1} arises due to P-O bending vibrations. Peak at 878 cm^{-1} may corresponds to condensed P-N units[41,42]. The broad band at 3416 cm^{-1} may be due to N-H stretching vibrations[43]. Peak in the range of 1650-1590 cm^{-1} corresponds to N-H bending vibrations. The material may possess lamellar type of structure, explained by the profile of the absorption band due to the $VOPO_4$ lattice vibration at 970 cm^{-1} was retained after the synthesis, suggesting the lamellar nature and intercalation compound was formed involving a V-P-O framework with the organic molecules[44]. The Vanadium phosphate layers may be sandwitched by n-propylamine (Figure 6)[45,46].

The Electron spin resonance spectrum (Figure 7) of Vanadium n-propylamino phosphate exhibits a typical characteristic eight-line hyperfine patterns originated from the interaction of an unpaired electron with nuclear spin (I = 7/2) of ^{51}V (natural abundance 99.8%). The well-resolved hyperfine patterns further indicate the paramagnetic center VO^{2+} is well dispersed in the sample. The EPR parameters ($g\ ll = 1.931$, $g \perp = 1.991$, $A\ ll = 180.5$ G, $A \perp = 69.5$ G) corresponds to V^{4+} in square pyramidal environment[47].

The UV-Vis diffuse reflectance spectrum (Figure 8) of Vanadium n-propylamino phosphate shows a band at 250 nm due to VO^{2+} species present in tetrahedral coordination[34].

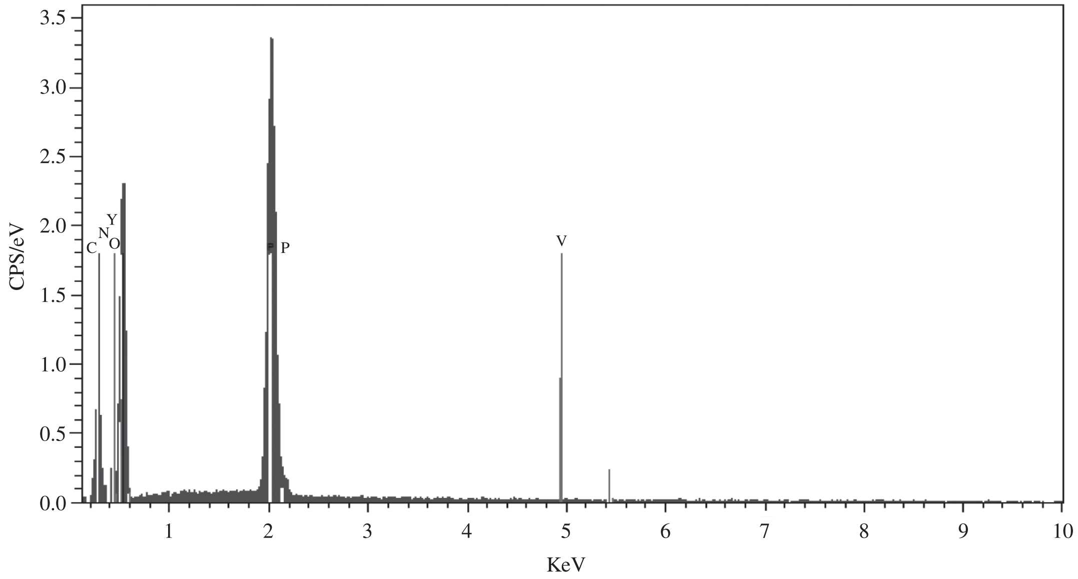


Figure 3. Energy dispersive X-ray analysis of Vanadium n-propylamino phosphate.

The band at 300-320 nm is in favour of high dispersion of V^{5+} ions in the lattice and due to (V=O) $(\pi)t_2 \rightarrow (d)e$ and $(\pi)t_1 \rightarrow (d)e$ electron transfer transitions[48] resulting from V^{5+} in tetrahedral environment. Hence, UV-Vis diffuse reflectance spectrum explains V^{4+} and V^{5+} ions are co-existed in the catalyst. Presence of a broad peak at 410-460 nm is due to charge transfer transitions of V^{5+} species (V=O) in square pyramidal geometry[49].

The X-ray photoelectron spectra (Figure 9a, b) of Vanadium n-propylamino phosphate shows the carbon 1s spectrum signal at 288 eV was attributed to carbon bonded to oxygen, Nitrogen and Hydrogen respectively[50]. The oxygen 1s spectrum shows signal at 534 eV is associated with the bridging oxygen of P-O-P bonds[51]. The binding energies for V-O-V and V=O structures have been reported to be closer to 531.6-530.9 and 530.3-529.9 eV, respectively[52] concludes the presence of V-O-P bonds in Vanadium n-propylamino phosphate. The N 1s signal shows peak around 400-404 eV correlated with the photo activity in Visible light[53] or may be due to presence of interstitial N_2 in Vanadium n-propylamino phosphate[54]. The Vanadium ion shows peak at 525 eV corresponding to binding energy of V $2p_{1/2}$ electron indicates Vanadium exists as V^{4+} oxidation state and the peak became broadened[55]. The V2p XPS spectrum indicates, Vanadium exists as V^{4+} and V^{5+} oxidation states in Vanadium n-propylamino phosphate catalyst. Vanadium n-propylamino phosphate catalyst possesses V^{5+} species with trace amounts of V^{4+} species. The P 2p binding energy shows a peak around 137 eV attributed to presence of phosphorous oxide P_2O_5[56] in Vanadium n-propylamino phosphate or related to presence of V-O-P compounds containing mono-, di- and poly- hydrogen phosphate anions[57].

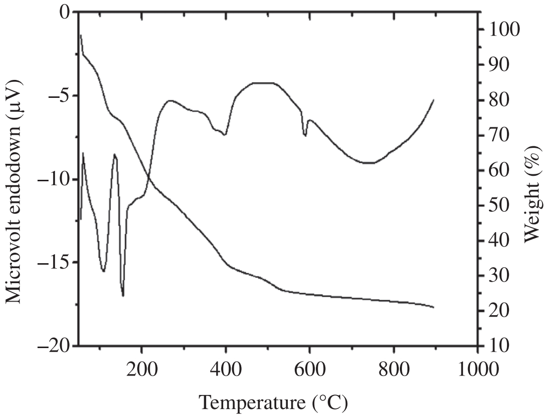


Figure 4. Thermogravimetry/Differential thermal analysis of Vanadium n-propyl amino phosphate.

Phosphorous solid state NMR spectroscopy is a powerful tool to distinguish different valence states of Vanadium surrounding the phosphorous atoms in different environments. ^{31}P MAS NMR spectrum (Figure 10) of Vanadium n-propylamino phosphate shows two ^{31}P peaks, with an intensity ratio of about 1:1 at 0 ppm is ascribed to the presence of phosphorous[58] in tetrahedral environment[59,60]. According to Bunker et al.[60] the peaks at 0 ppm is due to presence of PO_2N_2 tetrahedra. The ^{31}P MAS NMR spectrum explains two kinds of tetrahedra are formed simultaneously, at the expense of the PO_4 tetrahedral[61]. Phosphorous atoms at $VOPO_4$, in the neighborhood of V^{5+} species, leads to narrow ^{31}P MAS NMR signals in the range of ca. -22 to 4 ppm[62].

4. Catalytic Properties

4.1. *Influence of substituted aldehydes*

In order to confirm the versatility of the catalyst, the standard reaction was carried out by using various aromatic aldehydes in methanol and water. [Table 1, entries 1 to 7]. In all the cases, the reactions proceed smoothly to afford

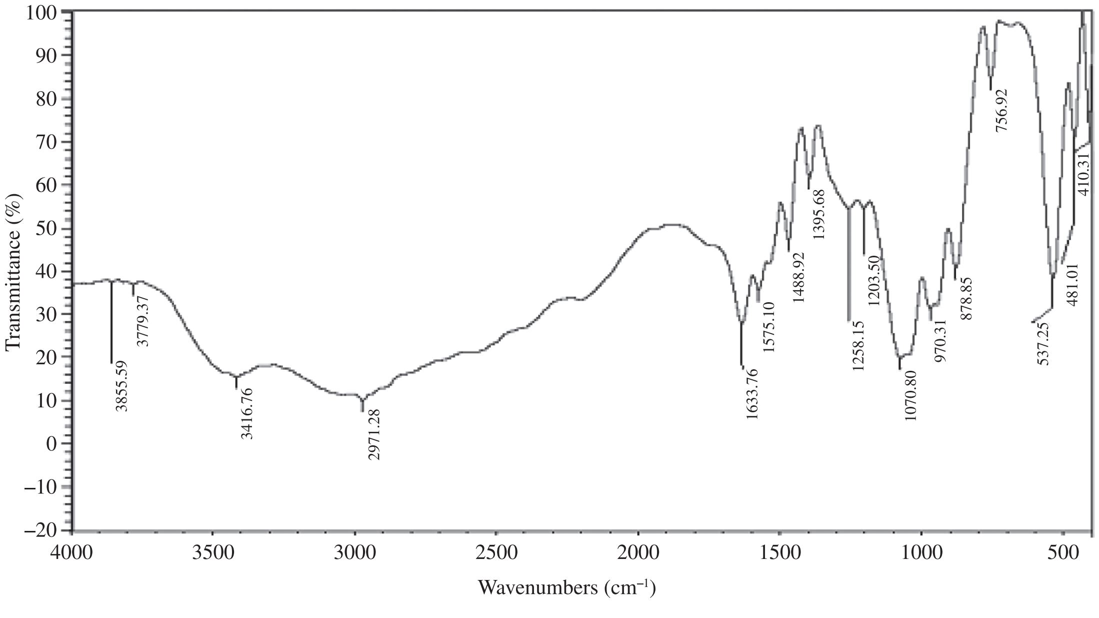


Figure 5. Fourier transform Infrared spectrum of Vanadium n-propylamino phosphate.

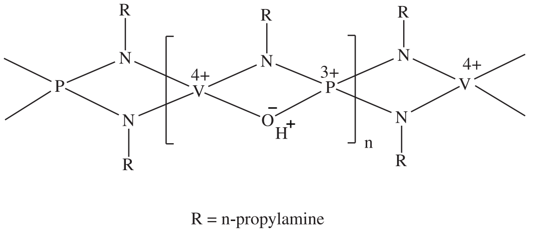


Figure 6. Structure of Vanadium n-propylamino phosphate catalyst.

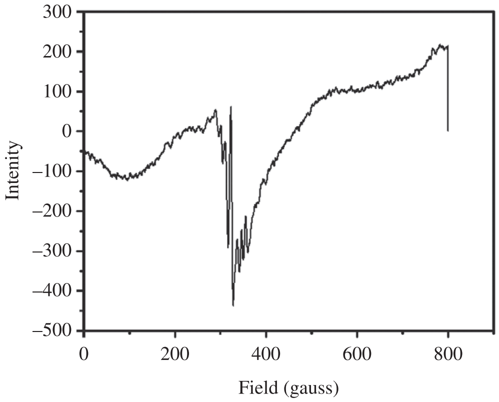


Figure 7. Electron spin resonance spectrum of Vanadium n-propylamino phosphate.

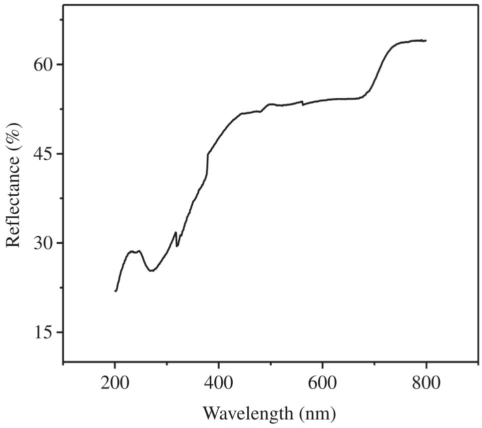


Figure 8. Ultraviolet - Visible diffuse reflectance spectrum of Vanadium n-propylamino phosphate.

the desired octahydroquinazolinone derivatives in 69-85% yields. The yields obtained were good to excellent without formation of side products. The aromatic aldehydes bearing electron withdrawing groups (p-NO_2, p-Br) reacted at faster rate compared with aromatic aldehydes substituted with electron releasing groups (p-methyl, p-hydroxyl. The corresponding products and yields were illustrated in Table 1.

4.2. *Influence of solvents*

Influence of solvents (Table 2) on the synthesis of octahydroquinazolinones is studied in presence of 0.05 g Vanadium n-propylamino phosphate have been monitored using solvents tetrahydrofuran, chloroform, water, acetonitrile, ethanol, methanol and methanol + water (1:1) at 60 °C. In comparison with other solvents, combination of methanol, water gave the products with higher yields. As protic solvents, methanol and water will solubilize dimedone and bring the reactants on the surface of the catalyst and enhance the yield. However, the reaction did not proceed in aprotic solvents like acetonitrile, chloroform and tetrahydrofuran.

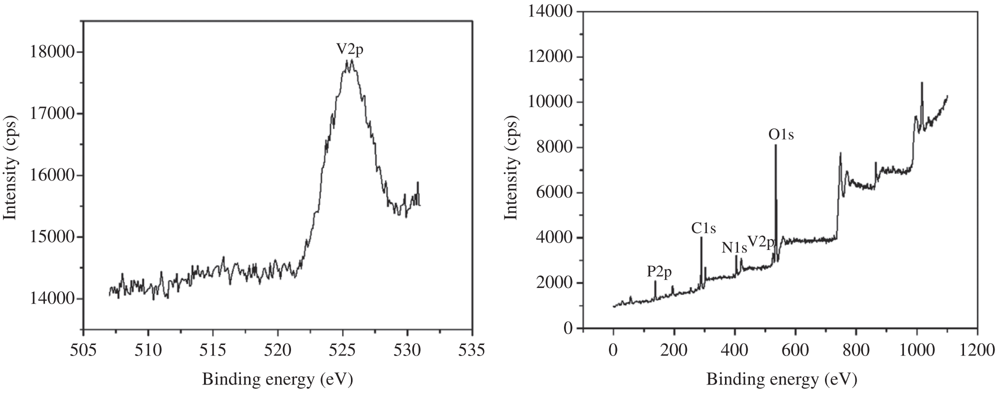
4.3. *Influence of the amount of catalyst*

In order to optimize the amount of Vanadium n-propylamino phosphate catalyst for the synthesis of octahydroquinazolinone derivatives, the reaction was carried out by varying the amount of catalyst from 0.03 g to 0.1 g (Table 3). With increase in amount of Vanadium

Table 1. Synthesis of various octahydroquinazolinones using methanol + water (1:1) solvent at reflux condition.

S. No.	R	Time (minutes)	M.P (°C)	Yield (%)
1	H*	90	290-293	30
2	H	90	290-293	85
3	4-Cl	120	>300	75
4	4-BrC_6H_4	90	>300	85
5	4-MeC_6H_4	120	>300	69
6	4-$NO_2C_6H_4$	90	304-305	73
7	4-OHC_6H_4	180	300-302	71

*$VOSO_4.5H_2O$ (catalyst); conditions: benzaldehyde (2 mmol); dimedone (2 mmol); urea (4 mmol); methanol + water (5 mL); 0.05 g vanadium n-propylamino phosphate catalyst.



(a) (b)

Figure 9. X-ray photoelectron spectras of Vanadium n-propylamino phosphate. (a) Vanadium ion (b) survey spectrum.

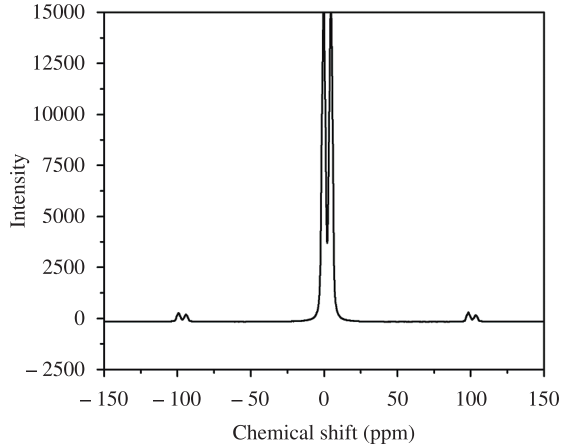
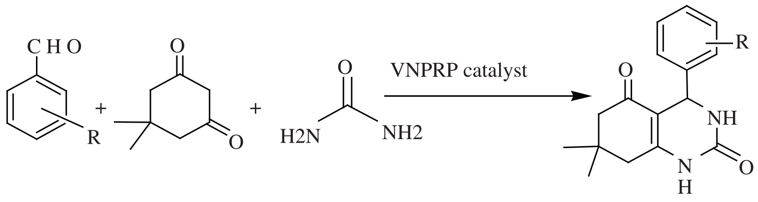


Figure 10. ^{31}P MAS NMR spectrum of Vanadium n-propylamino phosphate.

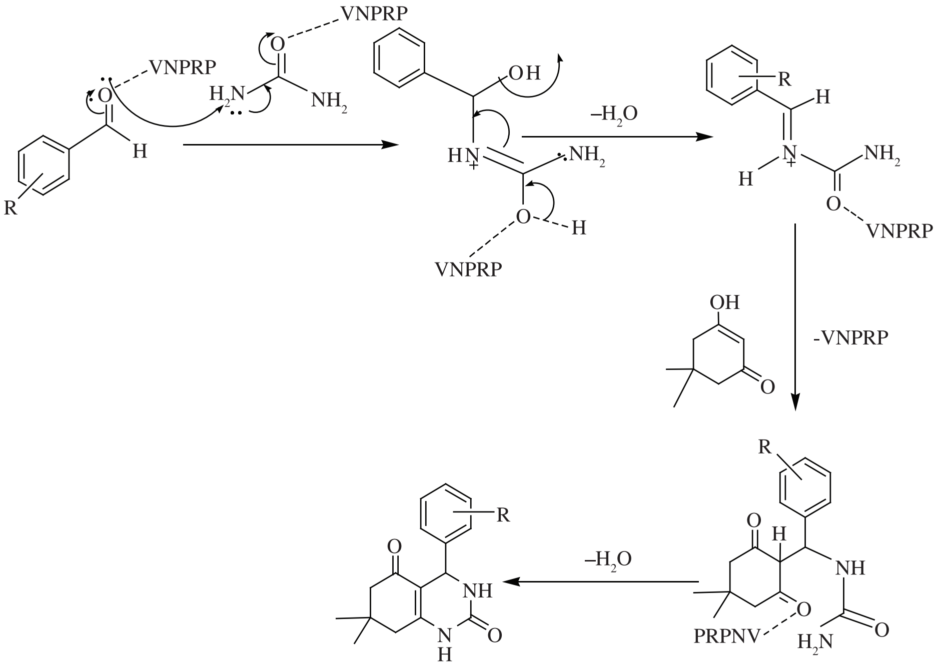
n-propylamino phosphate catalyst from 0.03 g to 0.1 g, no change in the reaction time was observed. The optimum amount of catalyst was found to be 0.05 g with respect to product yield and amount of catalyst. The yields of the products obtained were good to excellent without the formation of side products. The reactions carried out in the presence of Vanadium n-propylamino phosphate shows the formation of only octahydroquinazolinone derivatives.

4.4. *Recyclability of the catalyst*

Catalyst was recovered after the reaction by simple filtration, washed with dichloromethane, dried at ambient temperature and used for the next run. Recyclability of the catalyst (Table 4) for the standard reaction conditions at reflux temperature was investigated. The yields of the product obtained in the subsequent cycles are found to be 80, 65 and 50% (Table 4).



R = H, p-CH_3, p-NO_2, p-Br, p-OH, p-Cl
VNPRP = Vanadium n-propylamino phosphate.



R = H, OH, CH_3, Cl, Br, p-NO_2
VNPRP = Vanadium n-propylamino phosphate

Figure 11. Vanadium n-propylamino phosphate catalyst mediated synthesis of various Octahydroquinazolinones.

Table 2. Influence of various solvents on synthesis of octahydroquinazolinones.

S. No.	Solvent	Time (minutes)	Yield (%)
1	Methanol	90	80
2	Ethanol	90	70
3	Acetonitrile	90	65
4	Chloroform	90	NR
5	Tetrahydrofuran	90	NR
6	Methanol + Water (1:1)	90	85
7	Water	90	NR

Conditions: benzaldehyde (2 mmol); dimedone (2 mmol); urea (4 mmol); methanol + water (5 mL); 0.05 g vanadium n-propylamino phosphate catalyst; NR – No reaction.

4.5. *Mechanism*

The role of Vanadium n-propylamino phosphate catalyst is to activate the aldehyde by binding the oxygen atom of aldehyde with vacant orbital of Vanadium (Figure 11) to achieve the stable oxidation state. Low acidity and neutrality of Vanadium n-propylamino phosphate catalyst exhibit higher selectivity toward the synthesis of octahydroquinazolinones derivatives.

5. Conclusions

A novel Vanadium n-propylamino phosphate catalyst is synthesized and found to have lamellar structure with Vanadyl phosphate layers and n-propylamine sandwich. It was prepared from n-propylamine, Vanadyl sulphate and Orthophosphoric acid. It is characterized in detail by various spectral and physicochemical techniques. The characterization shows that the Vanadium is incorporated mainly as V^{4+} species. The catalytic applications of this material toward octahydroquinazolinones synthesis is established. Influence of various reaction parameters such as different solvents, various amounts of catalyst and aldehydes on Octahydroquinazolinones synthesis have been studied.

Table 3. Influence of the amount of catalyst on synthesis of octahydroquinazolinones.

S. No.	Amount (wt. (%))	Time (minutes)	Yield (%)
1.	0.03 g	90	60
2.	0.05 g	90	85
3.	0.07 g	90	70
4.	0.1 g	90	70

Conditions: benzaldehyde (2 mmol); dimedone (2 mmol); urea (4 mmol); methanol + water (5 mL); Vanadium n-propylamino phosphate catalyst.

Table 4. Reusability of the catalyst.

S. No.	Number of recycles	Time (minutes)	Yield (%)
1	Fresh	90	80
2	1	150	65
3	2	160	40

Conditions: benzaldehyde (2 mmol); dimedone (2 mmol); urea (4 mmol); methanol + water (5 mL); Vanadium n-propylamino phosphate catalyst (0.05 g).

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