

# Chapter - 10

## Vanadium-based Nanocomposites in Oxidation of Benzyl Alcohol

Biraj Das, Mukesh Sharma, Mitu Sharma and Arup J. Das

*Department of Chemical Sciences,  
Tezpur University 784028,  
Assam, India*

---

**Abstract**—*Selective oxidation of benzyl alcohol is considered as a challenging process due to the formation of various side products formed during the reaction. Different process has been developed to control the side product formation via controlling the free radical generation in the reaction. This chapter deals with the oxidation of benzyl alcohol with various vanadium-based catalysts.*

### **Introduction**

Oxide-based compounds are formed by a combination of an electropositive atom such as metal and oxygen atom. Transition metal oxides are recognized as an excellent material due to its versatile use in a different field such as in magnetic, optical, catalysis, energy sector, etc. These metal oxide also used in the photocatalytic reaction due to their suitable band gap. The activity of the metal oxides are found to be dependent on the structure of the material.<sup>1</sup> Recently, one of the fascinating fields in heterogeneous catalysis is the designing of

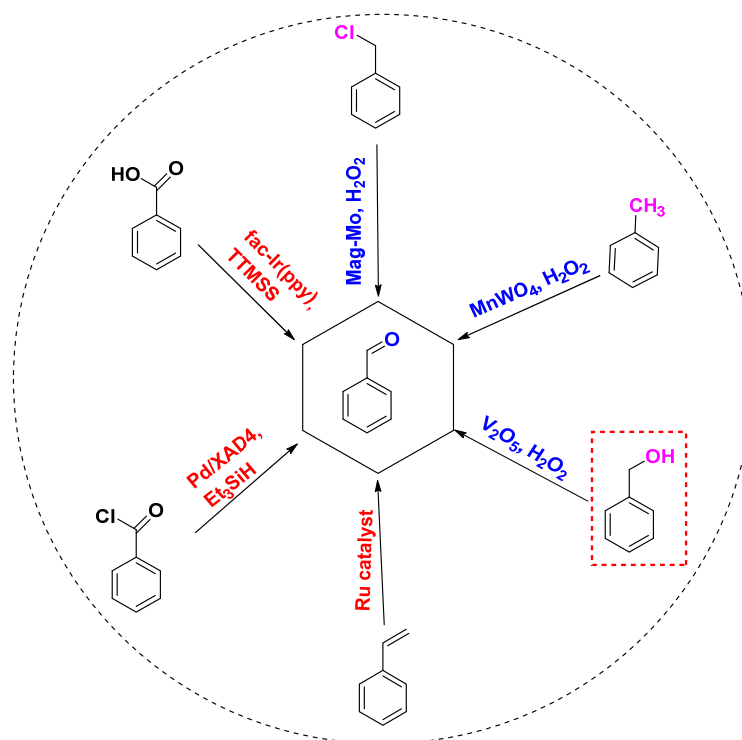
nanomaterial in the range of 1-100 nm. Different types of nanomaterials have been designed such as zero, one or two dimensions for various applications. As the physical and chemical properties were changes by tuning the size as well as the dimension of the nanomaterials.<sup>2</sup> The morphology of the material can be regulated by changing the different reaction parameters such as pressure, temperature, time, etc. The shape of the material also governed and controlled by introducing the surfactants or capping agent into the reaction system.<sup>3</sup>

Vanadium complex or vanadium-based oxides are widely used in different applications, and it can be synthesized using different ligands in order to mend the activity of the material. Recently, these types of materials are extensively applied as gas sensors, Li batteries, electrochemical, water splitting and as a catalyst in various organic transformations.<sup>4</sup> Different forms of vanadium oxides are synthesized such as  $V_2O_5$ ,  $VO_2$ ,  $V_2O_3$  and  $VO$  and some of the mixed valance vanadium is also synthesize with general formula  $V_nO_{2n-1}$ . The thermodynamically most stable phase of vanadium oxide is the  $V_2O_5$ . The  $VO_2$  phase usually transforms into  $V_6O_{13}$  and  $V_2O_5$ . Both the pure and mixed-phase of vanadium oxide has great potential in different industrial and fine chemical synthesis. This unique feature of vanadium-based compounds to form a variety of composites are linked to their phase transition ability at 340 K. Synthesis of a single-phase oxide and controlling of oxidation state of vanadium oxides are considered as challenging task in the field of material chemistry. Among all the units of vanadium oxides, the reversible phase

transition temperature of vanadium dioxide ( $\text{VO}_2$ ) is generally observed at 68 °C between monoclinic insulator to rutile metallic,  $\text{VO}_2(\text{M})$  and  $\text{VO}_2(\text{R})$ , respectively. The phase transition of  $\text{VO}_2$  leads to an alteration in the electrical and optical properties of the materials. The transition between  $\text{VO}_2(\text{M})$  and  $\text{VO}_2(\text{R})$  arises within 100 fs, and depends on the purity, size of the material and defects.<sup>5,6</sup>

$\text{V}_2\text{O}_5$  material has a high specific capacity, low toxicity and easy synthesis procedure which promotes it as an excellent cathode material. The commercial  $\text{V}_2\text{O}_5$  limits their application as a cathode material due to its low ionic diffusivity, intrinsic structural instability, as well as electrical conductivity that decreases after intercalation. The drawbacks associated with commercial  $\text{V}_2\text{O}_5$  could be overcome by designing of various diverse nanomaterials having morphology like nanorods, nanowire, nanobelts, etc. Vanadium oxides catalysts are also at times difficult to recycle and separate from the reaction. To overcome this problem, researchers are nowadays hybridizing different metal oxide-based catalyst with different support like carbon nanotube, silica, alumina, graphene, etc. Recently, carbon material such as multi-walled carbon nanotubes (MWCNTs) are recognized as an excellent support materials due to its high surface area, electrical conductivity, remarkable mechanical and thermal stability. Such support also reduces the poisoning effect during the course of reaction. Another advantage of MWCNTs is the synthesis of different functional group attached to the carbon atoms which alter its chemical and physical properties. The functional groups such as phenol, ketone, carboxylic acid,

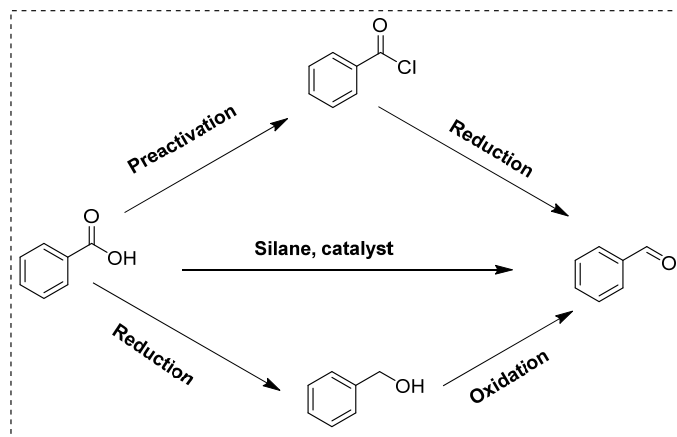
acid anhydride that contains oxygen atom are in general coordinated to CNT via control oxidation processes. The functional group which contains oxygen atom enhances the hydrophilicity of CNT in polar solvents. The carboxylic acid-functionalized CNT promotes the electrochemical reaction and decreases the activation energy and further boosts the electronic transfer of CNT materials. MWCNT was first synthesized by Iijima during the preparation of fullerenes and shows various applications in different fields like energy and gas storage material, electronic, sensing, and catalysis. MWCNTs are synthesized both industrially and academically using different processes such as arc discharge, laser ablation, flame synthesis, chemical vapour deposition, electrolysis, etc. As the diameter of the CNT increases with increasing the temperature, thus it can encapsulate more nanoparticles inside the tube. The oxygen-containing functional group such as carboxylic acids have also been used for coordination of different metal particles over the CNT surfaces. The COOH functionalized MWCNT is extensively used for anchoring of metal particles and in the absence of any functional group, the metal particles are formed over the surface of the MWCNT via impregnation process. In this process of hybridized material, only physical interaction between particle and support plays a role in the catalytic activity of the material and leaching were usually observed. The  $V_2O_5$  supported over MWCNTs composite shows high surface area and good conductive effect.<sup>7</sup>



**Scheme 1.** Synthesis of benzaldehyde from various starting materials.

Benzaldehyde is considered as an important derivatives precursor in the different reaction such as Schiff base synthesis, pharmaceutically important product synthesis, etc.<sup>8</sup> Benzaldehyde are synthesized via oxidation as well as a reduction processes from different substrates. In the reduction process, different costly metal catalysts are used in the presence of reducing agents. Some of the reported starting materials for the production of benzaldehyde via reduction process are from benzoic acid or acid chloride as depicted in Scheme 1. The reduction of benzoic acid is performed by reduction of benzoic acid to benzyl alcohol and further reduced to its corresponding aldehyde. Another two steps process is the

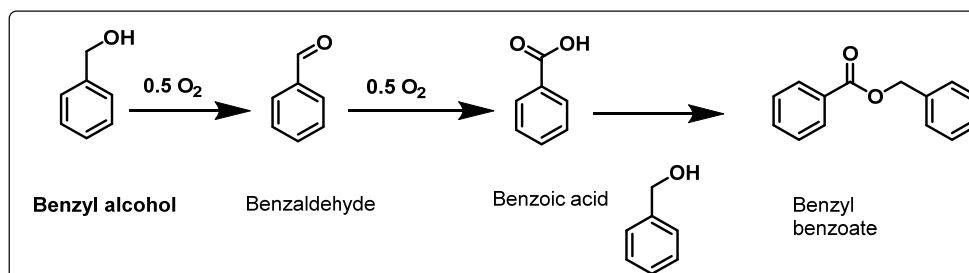
conversion of benzoic acid to its reactive form and thereby reducing it to benzaldehyde. One-step reduction of benzoic acid is also carried out in the presence of triethylsilane, or its derivatives are used as reducing agent, Scheme 2. Benzaldehyde can also be synthesized via oxidation of benzyl alcohol, toluene, chlorobenzene, styrene, etc.



**Scheme 2.** Routes for the synthesis of benzaldehyde from benzoic acid.

Selective oxidation of benzyl alcohol to their corresponding benzaldehyde in the presence of a catalyst is a desirable task from the organic chemist point of view. Benzaldehyde are usually synthesized via oxidation of benzyl alcohol using some oxidizing agents like molecular oxygen ( $O_2$ ), hydrogen peroxide ( $H_2O_2$ ) or TBHP, etc. in the presence of some metal catalyst. Oxidation of alcohols in the presence of  $H_2O_2$  requires lesser time than that of  $O_2$  but the main problem associated with  $H_2O_2$  is the command over the side products during the reaction. The major side products in alcohol oxidations are benzoic acid, benzyl benzoate, etc. occurred via the free radical mechanism and controlling the side reaction is

the major challenge for the researchers, Scheme 3. In the presence of  $\text{H}_2\text{O}_2$ , the recyclability of the metal complex is usually difficult as it forms peroxy-complex in the reaction mixture. Vanadium oxide-based catalysts are recognized as an active catalyst in benzyl alcohol oxidation process. In this chapter, oxidation of benzyl alcohol is discussed using various oxidizing agents.

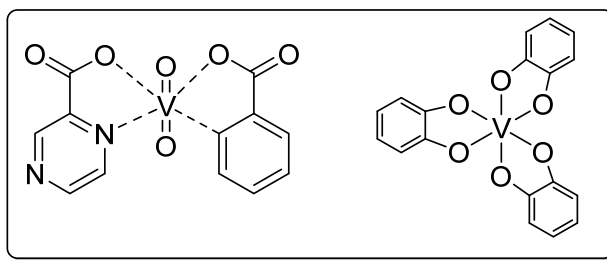


**Scheme 3.** Oxidation of benzyl alcohol to benzaldehyde and their possible byproducts.

### Homogeneous vs. heterogeneous catalyst

The alcohol oxidation reaction are generally performed with both homogeneous as well as heterogeneous catalysts. In the case of homogeneous catalysis, the reactant and catalyst are in the same phase. Different types of metal complexes have been already explored in alcohol oxidation. In most of the cases,  $\text{H}_2\text{O}_2$  is used as an oxidant in the oxidation process that dissolves the catalyst and make the reaction in homogeneous condition. These types of complex also shows excellent activity in alcohol oxidation reaction in the presence of  $\text{H}_2\text{O}_2$ . Some of the vanadium complexes employed in the oxidation of benzyl alcohol are depicted in Figure 1. Vanadium oxides such as  $\text{V}_2\text{O}_5$  or different vanadium oxide units are also employed in alcohol oxidation in the presence of molecular

oxygen as an oxidant. Similar to metal complex,  $V_2O_5$  also get dissolves in the presence of  $H_2O_2$  during the oxidation process. The recyclable of the catalyst can also be controlled in the presence of molecular oxygen.



**Figure 1.** Vanadium complex catalyst for alcohol oxidation reaction.

The advantages associated with homogeneous reactions are generally threefold

1. In most of the cases, the activity of the homogeneous catalyst is more effective in comparison to the heterogeneous catalysts.
2. The catalyst and reactant exist as a homogeneous mixture that eliminates the pore diffusion.
3. Investigation of the mechanism of the reaction in the homogeneous reaction is comparatively easier than the heterogeneous phase.

The disadvantage of homogeneous catalyst;

1. the catalyst and reactant mixture is in the same phase, i.e. liquid. The separation of the catalyst after the reaction is problematic and difficult and in most of the cases, the activity of the recycle catalyst are found to be very low.
2. The stability of the catalyst are very low than the heterogeneous catalyst.

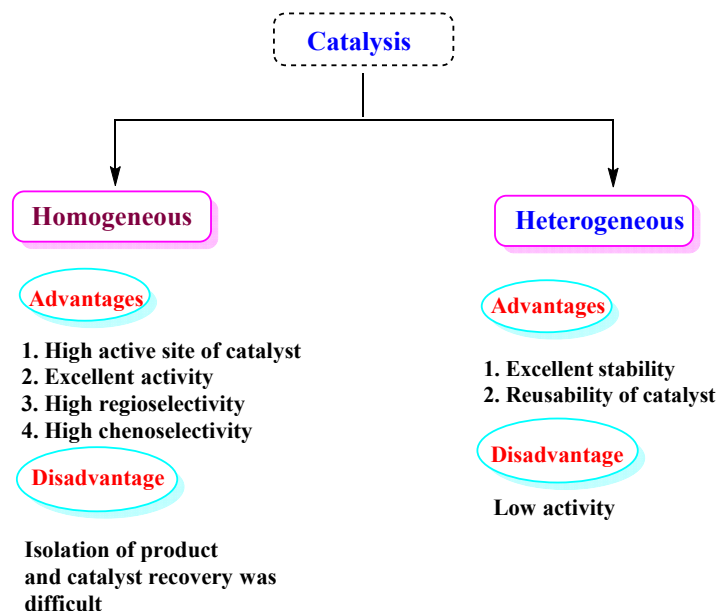


Advantage of the heterogeneous catalyst;

1. The stability of the catalyst are very high.
2. Catalyst can be reusable up to a large number of cycles.
3. Catalyst can be separated from the reaction mixture via filtration.

The disadvantage of heterogeneous catalyst;

1. It is difficult to know the mechanism of the reaction.



### Oxidation of benzyl alcohol

Oxidation of benzyl alcohol to benzaldehyde has been performed in the presence of  $V_2O_5$  catalyst using atmospheric oxygen as an oxidant at 100 °C. Up to 93% yield of benzaldehyde was obtained within 25 h under this condition. The reaction of benzyl alcohol oxidation is performed in the presence of 0.5 equiv.  $K_2CO_3$  as base. The presence of  $K_2CO_3$  increases the pH of reaction which restricts the undesired hemiacetal formation.<sup>9</sup> Li *et al.*

reported for the oxidation of benzyl alcohol in the presence of  $V_2O_5$  and  $H_2O_2$  as an oxidant under acidic condition. The reaction was performed in the presence benzyltriethylammonium bromide (BTEAB) which acts as a phase transfer agent (PTA) in the reaction. The benzaldehyde product was not observed at room temperature or under refluxing condition in the presence of  $V_2O_5$ , BTEAB, and  $H_2O_2$ . High yield of benzaldehyde was obtained after maintaining the pH of the reaction mixture at 4 using HCl,  $H_2SO_4$ , HBr, and  $H_3PO_4$  at 60 °C. When the pH of the reaction was further increased above 5, the formation of benzaldehyde was not detected. It is well known that  $V_2O_5$  in the presence of  $H_2O_2$  can be oxidized to vanadium peroxide species. They propose that  $VO(O_2)_2^-$  species behave as an oxidant as well as nucleophile in the oxidation reaction.<sup>10</sup> The oxidation of benzyl alcohol was also performed using  $VO(acac)_2$  supported in polyaniline using molecular oxygen as an oxidant. The reaction proceeded with high yield without using any external base during the reaction.<sup>11</sup> The use of  $H_2O_2$  in different oxidation reaction is considered as a green oxidant. The presence of peroxide with metal complex or oxide usually form peroxo like complex, and the progress of the reaction took place within a very short period of time. The oxidation reaction carried out in the presence of molecular oxidants was found to be a selective process, but it requires a long time in comparison to  $H_2O_2$ . Also, benzyl alcohol oxidation in presence of molecular oxygen usually required some co-catalyst such as DABCO, TEMPO, NHP, etc. Some of the vanadium-based catalysts are in Table 1.

The oxidation reaction in the presence of  $H_2O_2$  leads to a decrease in the stability of the material. Therefore, photocatalytic oxidation of benzyl alcohol can be considered as a useful protocol for the production of benzaldehyde. Semiconductor materials are also found to be suitable candidate and has several application in photocatalysis. Among different semiconducting materials,  $TiO_2$  has gained an ideal position as a photocatalyst due to its high stability and reactivity. But, the main drawback associated with  $TiO_2$  lies in the separation between photo induced electron and holes during the reaction. It has a high band gap, i.e. 3.2 eV which makes it a low response to visible light. Therefore, there is a high space for finding a suitable semiconductor material that can trap solar energy and can be used in different photocatalytic reaction. Among all the metal oxides, vanadium oxide is considered as an excellent semiconductor material in photocatalytic reaction due to its low band gap, i.e. 2.6 eV. The narrow band gap of the material makes it an active photocatalyst for the utilizing in both UV and visible spectrum of solar light.

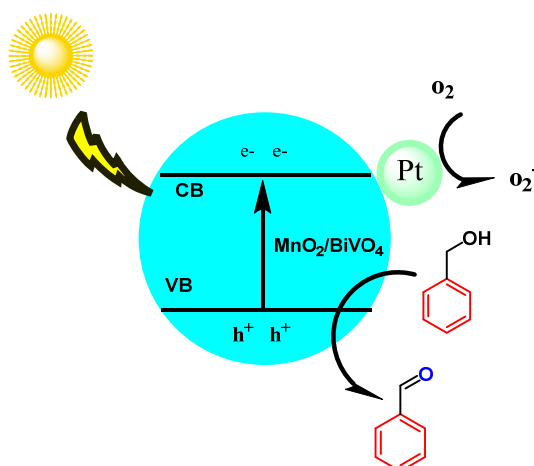
**Table 1.** Oxidation of benzyl with various vanadium-based catalysts.

Catalyst	Oxidant	Co-catalyst	Time	Yield (%)
$VO(acac)_2$	$O_2$	DABCO	6 h	96
$VOSO_4$	$O_2$	TEMPO	5h	-
$VO(acac)_2+Bu_4NCl$	$O_2$	NHP	18h	-
$VOPO_4$	$O_2$	TEMPO	12h	
$VO(acac)_2$	$Bu^tOOH$	-	3h	99
$(ODA)_4PMo_{11}VO_{40}$	$H_2O_2$	-	6h	-
$VOSO_4$	$O_2$	$NaNO_3$	2h	-
$((VO)_2P_2O_7)$	$H_2O_2$	-	4h	-

$(VO)_4(hpic)_4$	$O_2$	-	3h	62
$V_2O_5$	$H_2O_2$	$K_2CO_3$	6h	82
$V_2O_5$	$H_2O_2$	BTEAB	24h	84
$V_6O_{13}-\gamma-Al_2O_3$	$O_2$	-	16h	98
$VO(PO_3)_2$	TBHP	-	6h	96
$[(VO)_2(HL)(\mu-O)]$	$H_2O_2$	-	4h	80
$VO(acac)_2$	TBHP	-	6h	-

The main problem associated with the vanadium oxides material is the rapid recombination of electron and hole pair. As a result, there is a rapid decrease in the activity of the material in both the UV as well as the visible region of the spectrum. The activity of the material in photocatalytic reaction enhances by adopting two approaches. The first approach is the synthesis of nanoscaled material as a photocatalyst, as the migration distance of electron and hole to the reaction active sites decreases from the bulk in case of nanomaterial. Secondly, separation of the photogenerated electron and hole generate during the photocatalytic reaction by doping some co-catalyst into the metal oxides. Bismuth vanadate material can be used in different types of photocatalytic reaction due to its ability to absorb visible light of the solar spectrum. Moreover, the  $BiVO_4$  as photocatalyst has several advantages such as it possesses high stability, low cost, and low toxicity. Unsworth *et al.* synthesized bismuth vanadate nanoparticles via hydrothermal process. The material was used as a photocatalyst in the oxidation of benzyl alcohol using oxygen as an oxidant with 99% selectivity. The reaction was performed under LED light

having a wavelength of 470 nm. The nano-BiVO<sub>4</sub> shows higher activity than the bulk BiVO<sub>4</sub>.<sup>12</sup>



**Scheme 4.** Mechanism of photocatalytic oxidation of benzyl alcohol.

The photocatalytic oxidation of benzyl alcohol was also reported with some Pt and MnO<sub>2</sub> doped co-catalyst deposited on BiVO<sub>4</sub> material. The presence of Pt and MnO<sub>2</sub> decreases the reverse reaction as well as recombination or electron and hole. The recombination reaction is considered as the main limitation in the photocatalytic reactions. When the light falls on the surface of the catalyst, the photogenerated electron, and hole generated from the metal oxide reacts with O<sub>2</sub> and H<sup>+</sup> to form OH and superoxide radical. O<sub>2</sub> and H<sup>+</sup> are generated from the catalyst via water oxidation as the reaction proceeded in water. The OH and superoxide radical are the active species for alcohol oxidation as shown in Scheme 4. Verma *et al.* synthesized VO@g-C<sub>3</sub>N<sub>4</sub> for oxidation of benzyl alcohol under light. Graphitic carbon nitriles also act as good support for the metal and also controls the leaching of the metal during the reaction.<sup>14</sup>

Carbon material has high conductivity and mobility of electron which makes it an excellent support for the designing of various nanomaterials. In VO@g-C<sub>3</sub>N<sub>4</sub>, the deposition of metals in C<sub>3</sub>N<sub>4</sub> leads to enhance in the chemical as well as thermal stability of the material. In addition to various advantages, the activity of the material was also monitored by varying the composition of metal.

### **Conclusion**

In conclusion, the oxidation of benzyl alcohol has been discussed in various vanadium-based catalysts. The presence of H<sub>2</sub>O<sub>2</sub> decreases the reaction time but the regeneration of the catalyst was found to be difficult. Furthermore, oxidation of benzyl alcohol via photocatalytic process was found to be an excellent procedure to produce better activity than the other oxidation process.

### **References**

- [1] Gordon, T.R., Cargnello, M., Paik, T., Mangolini, F., Weber, R.T., Fornasiero, P. and Murray, C.B., Nonaqueous synthesis of TiO<sub>2</sub> nanocrystals using TiF<sub>4</sub> to engineer morphology, oxygen vacancy concentration, and photocatalytic activity. *Journal of the American Chemical Society*, **2012**, 134(15), 6751-6761.
- [2] Guo, T., Yao, M.S., Lin, Y.H. and Nan, C.W., A comprehensive review on synthesis methods for transition-metal oxide nanostructures. *CrystEngComm*, **2015**. 17(19), 3551-3585.
- [3] Malandrino, G., Finocchiaro, S.T., Lo Nigro, R., Bongiorno, C., Spinella, C. and Fragala, I.L., Free-standing copper (II) oxide

- nanotube arrays through an MOCVD template process. *Chemistry of Materials*, **2004**, *16*(26), 5559-5561.
- [4] Pradhan, M., Roy, A., Sinha, A.K., Sahoo, R., Deb, D. and Pal, T., Solid-state transformation of single precursor vanadium complex nanostructures to V<sub>2</sub>O<sub>5</sub> and VO<sub>2</sub>: catalytic activity of V<sub>2</sub>O<sub>5</sub> for oxidative coupling of 2-naphthol. *Dalton Transactions*, **2015**, *44*(4), 1889-1899.
- [5] Ningyi, Y., Jinhua, L. and Chenglu, L., Valence reduction process from sol-gel V<sub>2</sub>O<sub>5</sub> to VO<sub>2</sub> thin films. *Applied Surface Science*, **2002**, *191*(1-4), 176-180.
- [6] Berenguer, R., Guerrero-Pérez, M.O., Guzman, I., Rodriguez-Mirasol, J. and Cordero, T., Synthesis of vanadium oxide nanofibers with variable crystallinity and V<sup>5+</sup>/V<sup>4+</sup> ratios. *ACS Omega*, **2017**, *2*(11), 7739-7745.
- [7] Zhou, X., Wu, G., Wu, J., Yang, H., Wang, J., Gao, G., Cai, R. and Yan, Q., Multiwalled carbon nanotubes-V<sub>2</sub>O<sub>5</sub> integrated composite with nanosized architecture as a cathode material for high performance lithium ion batteries. *Journal of Materials Chemistry A*, **2013**, *1*(48), 15459-15468.
- [8] Li, H., Qin, F., Yang, Z., Cui, X., Wang, J. and Zhang, L., New reaction pathway induced by plasmon for selective benzyl alcohol oxidation on BiOCl possessing oxygen vacancies. *Journal of the American Chemical Society*, **2017**, *139*(9), 3513-3521.
- [9] Velusamy, S. and Punniyamurthy, T., Novel vanadium-catalyzed oxidation of alcohols to aldehydes and ketones under atmospheric oxygen. *Organic Letters*, **2004**, *6*(2), 217-219.
- [10] Li, C., Zheng, P., Li, J., Zhang, H., Cui, Y., Shao, Q., Ji, X., Zhang, J., Zhao, P. and Xu, Y., The dual roles of oxodiperoxovanadate both as a

nucleophile and an oxidant in the green oxidation of benzyl alcohols or benzyl halides to aldehydes and ketones. *Angewandte Chemie International Edition*, **2003**, 42(41), 5063-5066.

- [11] Reddy, S.R., Das, S. and Punniyamurthy, T., Polyaniline supported vanadium catalyzed aerobic oxidation of alcohols to aldehydes and ketones. *Tetrahedron Letters*, **2004**, 45(18), 3561-3564.
- [12] Unsworth, C.A., Coulson, B., Chechik, V. and Douthwaite, R.E., Aerobic oxidation of benzyl alcohols to benzaldehyde using monoclinic bismuth vanadate nanoparticles under visible light irradiation: Photocatalysis selectivity and inhibition. *Journal of Catalysis*, **2017**, 354, 152-159.
- [13] Jin, X., Li, R., Zhao, Y., Liu, X., Wang, X., Jiao, H. and Li, J., Spatial separation of dual-cocatalysts on bismuth vanadate for selective aerobic oxidation of benzyl alcohols to benzaldehyde under visible light irradiation. *Catalysis Science & Technology*, **2018**, 8(23), 6173-6179.
- [14] Verma, S., Baig, R.N., Nadagouda, M.N. and Varma, R.S., Selective oxidation of alcohols using photoactive VO@g-C<sub>3</sub>N<sub>4</sub>. *ACS Sustainable Chemistry & Engineering*, **2016**, 4(3), 1094-1098.