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RESEARCH ARTICLE

CATALYTIC OXIDATION OF SUBSTITUTED BENZYL ALCOHOLS TO ALDEHYDES USING $ZnWO_4$ NANOPARTICLES

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ABSTRACT

Nano $ZnWO_4$ particles have been successfully synthesized through sol-gel process. The size and morphology of $ZnWO_4$ nano particle can be controlled by adjusting the reaction time and temperature. The prepared nano $ZnWO_4$ shows band gap energy of 2.9 eV calculated from UV-DRS, Scanning Electron microscope (SEM), EDS, Transmission Electron microscope (TEM) and FT-IR spectra techniques. The resultant sample is a phase pure $ZnWO_4$. Further the Catalysis studies have been studied by the oxidation of functionalized benzyl alcohols to its corresponding aldehydes in good yields, and it was observed that the prepared $ZnWO_4$ nano particles have better catalytic efficiency.

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INTRODUCTION

Zinc tungstate is technologically important material and much attention due to its structure and reactivity. In recent years scientists shows much interest on synthesizing $ZnWO_4$ because it has wide variety of applications such as in photoluminescence (Vergados, 2012), magnetic properties (Zhang *et al*., 2002), laser hosts (Yang *et al*., 2012), flashing materials, humidity sensors (Qu *et al*., 2000), LED (Tomaszewicz *et al*., 2009), photocatalytic properties (Fu *et al*., 2006), phase change optical recording (Kuzmin *et al*., 1840) and nano ordered substrate materials (Atuchin *et al*., 2010). Also the $ZnWO_4$ extensively used in scintillators (Belli *et al*., 2011), photo anodes, electro optics as well as acoustic and optical fibres (Yoon *et al*., 2006; Bonanni *et al*., 1998). From the past few years $ZnWO_4$ has been prepared by different routes such as Czochralski method (Yang *et al*., 2008), co precipitation, solid-state metathesis (Huang and Zhu, 2007), hydrothermal method (Fu *et al*., 2006; Zhou *et al*., 2003; Fu *et al*., 2006; Huang and Gao, 2006; Siriwong *et al*., 2010), decomposition of polymeric complex (Ryu *et al*., 2004), Microemulsion method (Wu *et al*., 2007), solid state reaction (Wen *et al*., 2002), aqueous solution growth (Xiong *et al*., 2004), template method (Lin *et al*., 2008) and self propagating combustion method (Dong, *et al*., 2008). However, there are some drawbacks in the aforementioned methods such as long reaction cycles and elevated reaction temperatures. Sol-gel method was an easy method for preparing $ZnWO_4$ by controlling morphology and crystal growth orientation. Till now $ZnWO_4$ has been reported as a photocatalyst for the degradation of 4-chlorophenol, Methylene blue, Rhodamine B, Phenol, Crystal violet, Caramine indigo, Salicylic acid, Methyl orange and Acetaldehyde under UV irradiation around ~ 254 nm. The catalytic activity of $ZnWO_4$ has been reported by th4e oxidation of benzyl alcohol to benzaldehyde. In the present study, the synthesis of $ZnWO_4$ nanoparticles by a facile sol-gel process was reported at low temperatures. The measurements suggested that the photocatalytic property of the sample is related to the surface area, dimension of particles, and crystallinity. Moreover, the catalyst is relatively stable and can be reused. Here we report that different functionalized benzyl alcohols can be selectively oxidised to their corresponding

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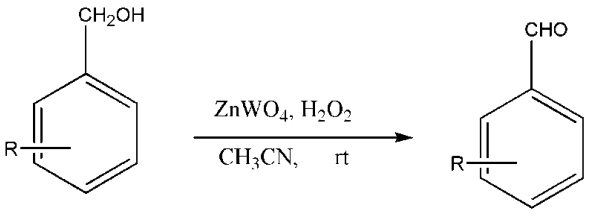
aldehydes using $ZnWO_4$ as catalyst in aqueous media. All the products thus obtained are in good yields.



MATERIALS AND METHODS

All the chemicals $Zn(NO_3)_2.4H_2O$ (Zinc Nitrate) (Merck grade), $Na_2WO_4.2H_2O$ (sodium tungstate) (Merck grade), Ethylene glycol (EG) (Merck grade), H_2O_2 (Merck grade), 3, 4-Dimethoxybenzylalcohol (Merck grade), 2-chloro benzyl alcohol (Merck grade), 4-hydroxy benzyl alcohol (Merck grade), 4-hydroxy 3-methoxy benzyl alcohol (Merck grade) and 3-Nitro benzyl alcohol (Merck grade) were purchased from Sigma Aldrich Pure Chemical Industries Co., Ltd and used without further purification. In a typical experiment, Nanoparticles of $ZnWO_4$ were prepared by dissolving 0.05 mmol of $Zn(NO_3)_2.4H2O$ and 0.05 mmol of $Na_2WO_4.2H_2O$ was dissolved separately in ethylene glycol (EG) under continuous stirring. After complete dissolution, the two mixtures were stirred at constant temperature for 24 h, and cooled to room temperature. Excess of sodium was removed by washing with distilled water and finally with absolute ethanol. The precipitate thus formed was dried at 70°C and calcinated at 300^0C for further characterization. $ZnWO_4$ Nano Particle assemblies were used for benzyl alcohol oxidation as a catalyst. In the reaction mixture, 0.5 mL of substituted benzyl alcohol was added with 25 mL of acetonitrile (as solvent) in a round bottomed flask. Then 100 mg of $ZnWO_4$ powder and 3 mL of 30% H_2O_2 solution were introduced into the mixture and heated at room temparature for about 12 h. The flask was fitted with aluminium foil to avoid the impinging of atmospheric oxygen. A usual almond smell reprents the formation of benzaldehyde, which stipulates the completion of reaction. After completion of the reaction, the products were purified and recrystallized with methanol. The final products were further confirmed by HPLC, ^{1}H NMR, FT-IR, and ^{13}C NMR studies. The aggregated $ZnWO_4$ particles were characterized using different spectroscopic tools such as UV-DRS, Scanning Electron microscope (SEM), Transmission Electron microscope (TEM) and FT-IR spectra techniques.

RESULTS AND DISCUSSION

The morphology and Phase purity of the calcined and washed powder was investigated with XRD patterns of $ZnWO_4$ photocatalysts were recorded by a PANalytical- X' Pert PRO, Japan 4 X-ray diffractometer operated at room temperature, using Nickel filtered Cu-K_α radiation (λ= 1.54059 Å), over the range of 10-80° with a scan rate of 2° min^{-1}. UV-Vis DRS was performed on a Hitachi (U-3010) between 200 to 800 nm range and $BaSO_4$ was used as a reference. Spectral grade $BaSO_4$ was taken as reference for the reflectance spectra. Micro structural investigations of the samples were performed on the powders of the samples using SEM (JEOL-JSM-6610LV, Tokyo, Japan). Fourier transform infrared spectra (FT-IR) were recorded on a Perkin-Elmer 1600 FT-IR spectrometer with a KBr disk.

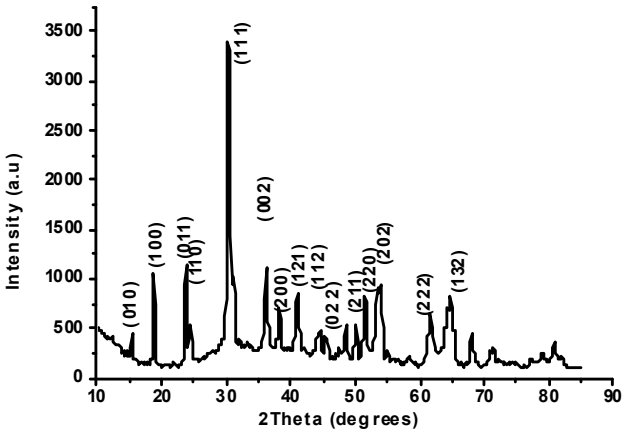


Figure 1. XRD pattern of nano $ZnWO_4$ calcined at 300^0C for 3hrs

Fig. 1(a) shows the XRD pattern of $ZnWO_4$ nanoparticles at 70^0C followed by calcination at 300^0C for 3 hrs. All the peaks in XRD pattern indicates the structure $ZnWO_4$ nanoparticles could be to monoclinic wolframite in terms of JCPDS Card Files: 88-0251 and 14-0676, respectively. A little dimension of grain was observed due to appearance of some wider diffraction peaks. The calculated lattice constants of the catalyst were a= 4.697 A^o, b= 6.041 A^o, c= 4.925 A^o represents nano $ZnWO_4$ has phase pure monoclinic.

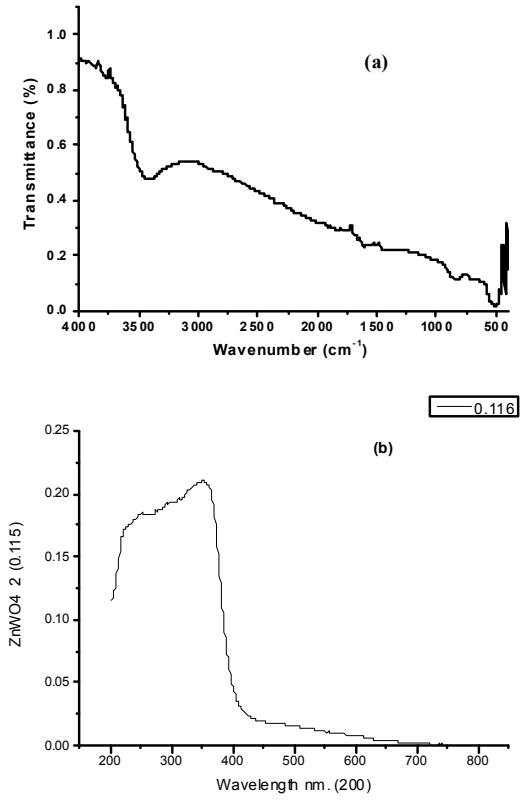


Figure 2 (a) FT-IR image of $ZnWO_4$ (b) UV-vis diffuse reflectance spectrum of $ZnWO_4$ powder

The FT-IR spectrum of $ZnWO_4$ particles is shown in Fig. 2(a). All the observed peaks are in good agreement with earlier reports (Huang *et al*., 2007). The bands at 833 cm^{-1} and 870 cm^{-1} are attributed to streching mode of W-O in WO_6 octahedra and the bands at 463cm^{1} and 585 cm^{1} are attributed to the bending vibrations of W–O. The bands at 532 and 620 cm^{-1} represents the symmetric vibrations of bridged oxygen atoms of Zn-O-W. The absorption bands at 430 and 465 cm^{-1} are due to symmetric and asymmetric deformation modes of W-O bonds and Zn-O bonds in WO_6 and ZnO_6 octahedra respectively. Other bands at 3600 and 1660 cm^{-1} are due to H-streching vibrations of ethylalcohol and H–O–H bending vibrations. Photoabsorptive ability studies of the catalyst were evaluated by UV-DRS shown in Fig. 2(b). From the figure it is noted that an absorption edge in the region close to 420 nm was observed and from which the estimated band gap of the synthesized $ZnWO_4$ powder is calculated to be 2.9 eV. For nano structured powders a direct band gap of 3.31 eV and an indirect band gap of 3.8 eV and for $ZnWO_4$ single crystals 3.9 - 4.4 eV were reported.

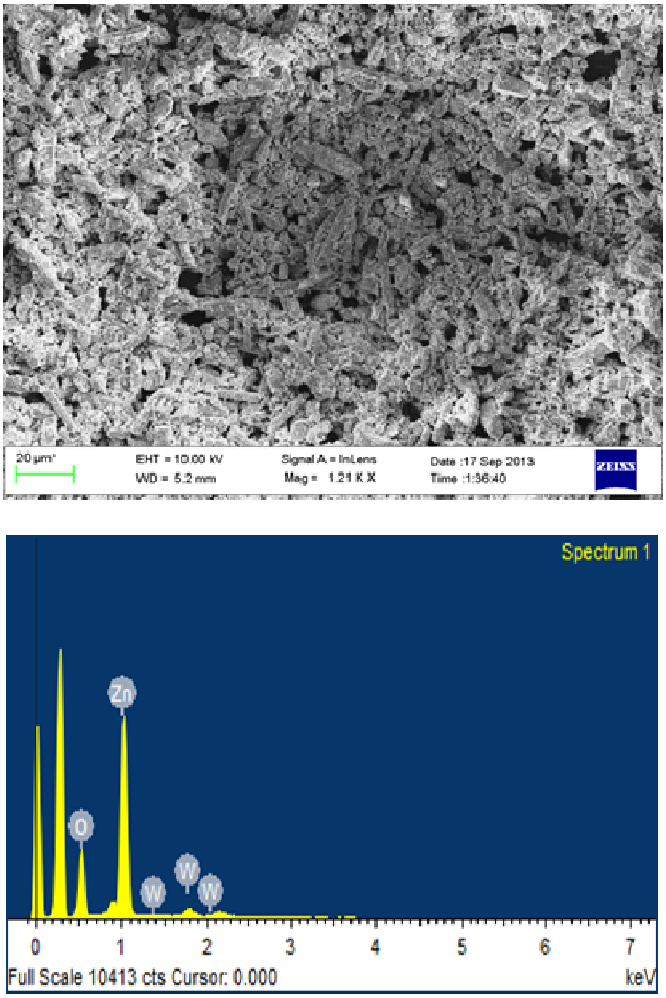


Figure 3 (a) SEM image of $ZnWO_4$ (b) EDS of $ZnWO_4$

Fig. 3(a) represents the SEM image of the prepare $ZnWO_4$ nanoparticles. The morphologies and microstructure were investigated and it was found that the nano $ZnWO_4$ particles are in spherical shape with uniform Particle size. Fig 3(b) represents EDS spectrum of $ZnWO_4$.

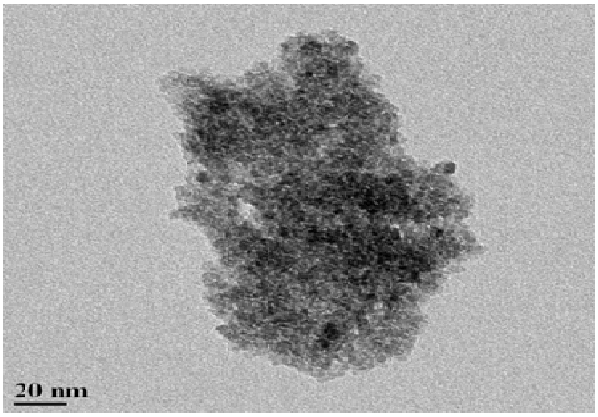


Figure 4. TEM image of $ZnWO_4$

Fig. 4 shows the TEM image of the prepared $ZnWO_4$. From TEM image it was observed that, all the particles are in spherical shape with uneven size. The average crystallite size of the $ZnWO_4$ particles are in the range of about 5-7 nm. Based on the above results it can be concluded that the prepared ZnWO4 particles are in nanometer range with spherical shape.

Table 1 represents the oxidation of Substituted alcohols to aldehydes. It was noticed that the electron withdrawing substituent's on the aromatic ring give moderate to good yields. The presence of nitro substitution on the aromatic ring gave high yields rather compared to electron releasing groups according to mesomeric effect. In IR spectra these compounds showed characteristic absorption at a range 700-2940 cm-1. In 1H NMR spectral studies a chemical shift for CHO group ain the range of 9.5- 9.836 ppm for all the compounds were observed.

Spectral data of the compounds

1. 4-hydroxy 3- Methoxybenzaldehyde

IR (KBr pellet) : 3300 cm-1, 3100 cm -1, 1660 cm-1, 1600 cm-1, 1100 cm-1; ^{1}H NMR (400 MHz/CDCl3) δ ppm : 7.17(1H,d), 7.32(1H,s), 6.72 (1H, d), 9.87 (1H, s), 3.62 (1H, s) ; 13C NMR (22.5 MHz/CDCl3) δ ppm : 189.2, 149.2, 148.3, 130.1, 117.2, 116.7, 55.5**;** Mass-ESI: 151 (M).

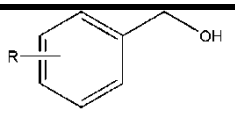
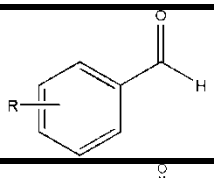
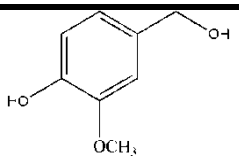
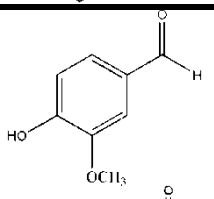
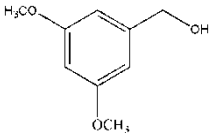
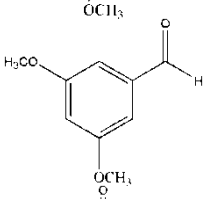
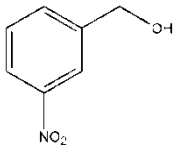
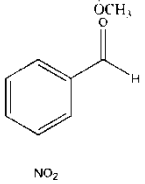
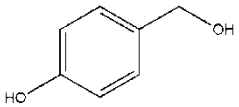
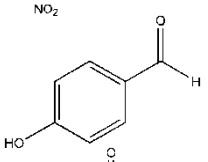
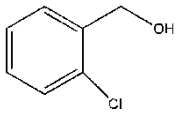
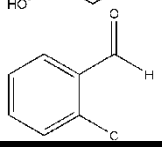
2. 3, 4-Dimethoxybenzaldehyde

IR (KBr pellet) : 3250 cm-1, 3100 cm-1, 1650 cm-1, 1600 cm-1, 1250 cm-1; ^{1}H NMR (400 MHz/ CDCl3) δ ppm: 9.78 (1H, s), 6.70(1H, d), 6.56(1H, s), 6.80(1H, d), 6.38 (2H, s), 3.79(6H, s); ^{13}C NMR (22.5 MHz/CDCl3) δ ppm : 189.0, 167.40, 152.00, 150.20, 126.50, 120.00, 116.10, 107.50, 55.25; Mass-ESI: 166 (M).

3. 3-Nitro benzaldehyde

IR (KBr pellet) : 3350 cm-1, 3050 cm-1, 1650 cm-1, 1600 cm-1, 1350 cm-1; ^{1}H NMR (400 MHz/ CDCl3) δ ppm: 9.78 (1H, s), 8. 29 (1H, d), 8. 29(1H, t), 8.10(1H, d), 8.45(1H, s); ^{13}C NMR (22.5 MHz/CDCl3) δ ppm: 189.0, 167.50, 150.20, 139.50, 127.00, 120.30; Mass-ESI: 152 (M).

Table 1. Oxidation of substituted Benzyl alcohols

S.No			Time (hrs)	Yield (%)
1			**14**	**78**
2			**15**	**76**
3			**8**	**92**
4			**12**	**80**
5			**9**	**85**

4. 4-Hydroxy benzaldehyde

IR (KBr pellet) : 3100 cm-1 3200 cm-1, 3300 cm-1 1630 cm-1, 1600 cm-1, 1200 cm-1; ^{1}H NMR (400 MHz/ CDCl3) δ ppm : 9.85(1H, s), 7.85(1H, d), 7.85(1H, d), 6.82(1H, d), 6.10 (1H, s), 5.15(1H, s); ^{13}C NMR (22.5 MHz/CDCl3) δ ppm : 189.0, 167.12, 160.00, 127.16. 125.96, 116.00; Mass-ESI: 137 (M).

5. 2-Chlorobenzaldehyde

IR (KBr pellet) : 3350 cm-1, 3050 cm-1, 1540 cm-1, 1610 cm-1, 610 cm-1; ^{1}H NMR (400 MHz/ CDCl3) δ ppm : 10.35 (1H, s), 7.79 (1H,d), 7.24(1H,d), 7.48(1H, s), 7.49 (1H, s); ^{13}C NMR (22.5 MHz/CDCl3) δ ppm : 190.0, 137.1, 136.22, 132.10, 130.00, 128.5, 127.1, 129.4; Mass-ESI: 139 (M).

Conclusions

$ZnWO_4$ nanoparticles have been successfully synthesized by sol-gel method at low temperature. The products were characterized by X-ray powder diffraction (XRD), Scanning Electron Microscope (SEM), Fourier infrared spectrum (FT-IR) and Transmission Electron Microscope (TEM). Moreover nano $ZnWO_4$ has been applied as catalyst for the conversion of Substituted benzyl alcohols to their corresponding aldehydes with good yields.

Acknowledgements

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