**Aerobic oxidation of benzyl alcohols to benzaldehydes using monoclinic bismuth vanadate nanoparticles under visible light irradiation: photocatalysis selectivity and inhibition**

Christopher A. Unsworth, Ben Coulson, Victor Chechik and Richard E. Douthwaite

Department of Chemistry, University of York, Heslington, York, YO10 5DD (UK)

E mail: richard.douthwaite@york.ac.uk

**Abstract**

Monoclinic bismuth vanadate nanoparticles (nan-BiVO4) have been used for the selective photo-oxidation of benzyl alcohols (13 examples) to benzaldehydes under visible light irradiation using dioxygen as oxidant. Illumination with a blue LED (λmax = 470 nm) gave yields more than 30 times greater than bulk BiVO4 with > 99% selectivity for several cases. Photo-oxidation of PhCH2OH/PhCD2OH isotopomers gave a kinetic isotope effect of 1.3 indicating that C-H bond activation is not the rate determining step in contrast to other reported photocatalysts including TiO2 and carbon nitride. Collectively, structural characterization, spectroscopic, and reactivity data are correlated with the greater surface area of nan-BiVO4 compared to bulk BiVO4. Furthermore, conversion is shown to be limited as reaction progresses. Control experiments indicate that photo-oxidation is retarded by product aldehyde and that trace amounts (< 1%) of the corresponding benzoic acid, from over-oxidation, result in significant reduction in conversion.

Keywords

Photocatalyst; metal oxide; oxidation; mechanism; product inhibition; catalyst poisoning.

**1. Introduction**

Photocatalysis offers the opportunity to drive chemical reactions using solar radiation as a free and clean energy source. Heterogeneous photocatalysis has been predominantly applied to the unselective photooxidation of atmospheric and aqueous organic pollutants using metal oxide photocatalysts and dioxygen.[1-5] There are also significant opportunities to apply heterogeneous photocatalysis to selective synthetic chemistry, however many challenges remain in addition to selectivity, including the use of reusable earth abundant catalysts that function under visible light irradiation.

Aldehydes are valuable as food additives, fragrances, and synthetic intermediates.[6-9] They are often produced from the corresponding alcohols, via chemical oxidation reactions which employ stoichiometric oxidants such as chromate and permanganate which generate considerable waste,[10-13] or precious metal complex catalysts at elevated temperatures when using dioxygen as oxidant.[14-16] In contrast, heterogeneous photocatalysis operates at room temperature, in air using dioxygen, and catalysts can be recycled easily. However, there remain challenges to achieving a viable process including the use of visible light, reducing electron-hole recombination, and improving chemoselectivity principally reduced by over oxidation. For decades, titanium dioxide has been investigated as a photocatalyst to selectively convert benzyl alcohol to benzaldehyde under UV-light irradiation in a dioxygen atmosphere.[1, 17-19] The common polymorphs of TiO2 have wide bandgaps of ca. 3.0 (rutile) and 3.2 eV (anatase) preventing visible light absorption and under UV irradiation over-oxidation commonly occurs with significant, competitive formation of carboxylic acids.[20]

Several approaches have been pursued to increase spectral match to visible light whilst maintaining selectivity. For example, molecular ruthenium photocatalyst complexes have been immobilised on metal oxide supports in order to create a selective system for benzyl alcohol oxidation, however these systems require the use of sacrificial electron donors.[21, 22] Visible-light absorbing materials such as graphitic carbon nitride (g-C3N4 bandgap = 2.7 eV) and bismuth tungstate (Bi2WO6 bandgap = 2.8 eV) are capable of selective benzyl alcohol oxidation to benzaldehyde but with low conversion of 9 and 30% respectively after several hours of irradiation using an intense (300 W) Xe arc lamp light source.[23, 24] Photoactive semiconductor composites have also been investigated, primarily to decrease electron-hole recombination. These include nanocomposites of bismuth tungstate and reduced graphene oxide,[25] tungsten oxide loaded with a palladium oxide cocatalyst,[26] and cadmium sulphide nanorods with an amorphous titania coating which selectively oxidizes benzyl alcohol to benzaldehyde,[27], but all require complex and multistage synthetic methods for their preparation.

Monoclinic bismuth vanadate, BiVO4, has a band gap of 2.4 eV and has been used extensively for visible light photoelectrochemical water oxidation under bias.[28-32] Of relevance to this work bismuth vanadate has been used for the selective photocatalytic oxidation of benzyl amines to their corresponding imines (up to 97% conversion, 91% selectivity in 7 hours) using a broad band Xe lamp and a 420 nm filter.[33]

Our motivation for this work was to investigate photocatalytic synthesis using inexpensive LED visible light sources and earth abundant metal oxides for selective oxidation. In related visible light photocatalysis with metal oxides, low conversions are often observed and attributed to rapid charge carrier recombination which is common for metal oxides. Therefore, we also targeted nanostructured materials to increase the probability of charge carrier diffusion to the surface. The key features which control the selectivity of heterogeneous photocatalytic oxidation are also poorly understood.

Herein we report the synthesis of BiVO4 nanoparticles (nan-BiVO4) using a simple hydrothermal method and their application to the aerobic photooxidation of benzyl alcohols to benzaldehydes. Illumination with a blue LED gave benzaldehydes in high yield and selectivity. The activity of nan-BiVO4 under these conditions was shown to be 10 times greater than titanium dioxide and 30 times greater than bulk BiVO4. Importantly, it was also observed that conversion is limited by even small quantities of benzoic acid and that the photoreaction is significantly inhibited by over-oxidation.

**2. Experimental**

*2.1. Materials*

Bismuth nitrate pentahydrate (98%), ethylenediaminetetraacetic acid (EDTA, 98.5%), 4-methoxybenzyl alcohol (98%), 4-methylbenzyl alcohol (98%), 4-ethylbenzyl alcohol (99%), 4-isopropylbenzyl alcohol (97%), biphenyl-4-methanol (98%), 4-chlorobenzyl alcohol (99%), 4-bromobenzyl alcohol (99%), 4-iodobenzyl alcohol (97%), 4-trifluoromethylbenzyl alcohol (98%), 4-nitrobenzyl alcohol (99%), 4-hydroxybenzyl alcohol (99%), benzyl alcohol (99%), 4-nitrobenzaldehyde (99%), 4-methoxybenzaldehyde (99%), methyl 4-formylbenzoate (99%), 4-(trifluoromethyl)benzaldehyde (98%) and cuminaldehyde (98%) (all Sigma-Aldrich), acetonitrile (Fisher Scientific), methyl (4-hydroxymethyl) benzoate (99%) and 4-acetamido benzyl alcohol (97%) (Alfa Aesar), ammonium metavanadate (98%) (Riedel-de Haen) and P25 titanium dioxide (Degussa), were used as received.

*2.2. Characterisation*

Powder X-ray Diffraction (PXRD) data was acquired using a Bruker-AXS D8 Advance instrument fitted with a Lynxeye detector and acquired with Cu Kα radiation between 10- 70° 2θ with a 0.02° step size. UV-vis Diffuse Reflectance Spectra (DRS) were recorded on an Ocean OpticInc. HR2000+ High Resolution Spectrometer. Scanning Electron Microscopy (SEM) was performed on a FEI Sirion scanning electron microscope and a JEOL Schottky field emission scanning electron microscope, at an accelerating voltage of 15 kV. Bulk BiVO4 samples were prepared by spreading a small amount of powder onto carbon tape mounted on an aluminium stub.Bismuth vanadate nanoparticles samples were dispersed in ethanol (1 mg mL-1), this dispersion was dropped onto a copper TEM grid and left at room temperature to allow the solvent to evaporate. Brunauer, Emmett and Teller (BET) N2 surface area analysis was performed on samples dried under nitrogen for 6 hours at 80 °C, and nitrogen adsorption isotherms were measured at 78 K on a Micromeritics Tristar 3000. 1H Nuclear magnetic resonance (NMR 400MHz) spectra were recorded on a JEOL ECX400 and ECS400 spectrometers at room temperature. Chemical shifts are referenced to the deuterium lock of residual solvent. Gas Chromatography (GC) was performed on an Agilent/HP 6890, with an injection volume of 1 μL, using helium as a carrier gas at 1 mL min-1, a flame ionisation detector at 250 °C, and Chrompack DB-5ms column between 90 and 300 °C with ramp rate 20 °C min-1. Time resolved photoluminescence was performed on an Edinburgh Photonics FLS 980 spectrometer, irradiating a 1 mg mL-1 acetonitrile dispersion with an Edinburgh instruments picosecond pulse light emitting diode, λ = 380 nm. Photocatalysis was carried out using an Et Lumiere 30 W blue LED array, λmax = 470 nm, λrange = 400 to 560 nm, with an irradiance of 245 mW cm-2 measured using a ITL 1400-A Radiometer Photometer at a distance of 2 cm.

*2.3. Catalyst preparation*

Synthesis of BiVO4 nanoparticles (nan-BiVO4): nan-BiVO4 was prepared by a modified literature method.[34] Bismuth nitrate pentahydrate (4.85 g, 10 mmol) and EDTA (2.93 g, 10 mmol) were added to 2M nitric acid (100 mL) and stirred for 30 min until clear. Ammonium metavanadate (1.17 g, 10 mmol) was added to this solution and stirred for 2 h giving a green-yellow solution. The solution was heated at 90 °C for 6 h in a Teflon-lined autoclave and after cooling to room temperature the resulting mixture was centrifuged at 4000 rpm for 30 min to yield a yellow powder, which was washed alternately with distilled water and ethanol and then dried overnight at 60 °C. Yield = 0.420 mg (13.0 %).

Synthesis of bulk BiVO4:[35]Bismuth nitrate pentahydrate (5.53 g, 12 mmol) and ammonium vanadate (1.41 g, 12 mmol) were dissolved in conc. nitric acid (20 mL) and 5M NaOH (20 mL) separately. After stirring for 30 min, these solutions were mixed forming a yellow precipitate. The resulting mixture was placed in 3 x 23 mL Teflon-lined autoclaves and heated to 240 °C for 16 h. After cooling to room temperature the resulting mixtures were combined and centrifuged at 4000 rpm for 30 min to yield a yellow powder, which was washed with distilled water and then dried overnight at 60oC. Yield = 1.34 g (34.5 %).

*2.4. Photocatalytic reactions*

Bismuth vanadate (32.3 mg, 100 µmol) was added to a Schlenk flask containing benzyl alcohol stock solution (1 mL, 0.1 mmol in acetonitrile) and acetonitrile (9 mL). The mixture was left to stir for 30 min to disperse the catalyst under a dioxygen atmosphere via a balloon. The mixture was then irradiated with a 30 W blue LED array at a distance of 2 cm with an irradiance of 245 mW cm-2. The mixture reached ca. 40 °C by the end of the reaction and after irradiation, the catalyst was removed using centrifugation at 4000 rpm for 30 min. For GC analysis, 1 mL of supernatant was taken and 1 μL injected. For NMR analysis, the supernatant was reduced in volume using a rotary evaporator at 65 mbar at 20 °C, and the residue dissolved in d6-DMSO containing maleic acid as an internal standard.

**3. Results and Discussion**

*3.1 Synthesis and Characterisation of nan-BiVO4*

Photocatalytic efficiency is reduced by electron-hole recombination processes which can be partly characterized by the bulk diffusion length of holes and electrons. By reducing the photocatalyst particle size, bulk electron-hole recombination can be reduced hence improving the efficiency of the catalyst. Although surface recombination is also significant, an increase in the surface area often gives an increase in activity due to the increasing availability of sites for substrate adsorption and chemical reaction. The smaller dimensions of high surface area materials also increase the probability of bulk diffusion of electrons and holes to the surface. For BiVO4 the limiting hole diffusion length is ca. 100 nm[36] and therefore particles of smaller dimension than 100 nm were targeted to reduce the probability of bulk electron-hole recombination.

Here bismuth vanadate nanoparticles (nan-BiVO4) were synthesised under hydrothermal conditions using a modified literature procedure.[34] Other methods have been used to prepare BiVO4 to maximise surface area. These include the solvothermal synthesis of free hollow BiVO4 spheres,[37] combustion synthesis of BiVO4 nanoparticles,[38] spray pyrolysis to form BiVO4 thin films[31] and the synthesis of nanoporous BiVO4 electrodes through electrochemical deposition of BiOI and a subsequent reaction with VO(acac)2.[28] These syntheses give materials exhibiting surface areas in the range 3.0 - 31.2 m2 g-1. However, to our knowledge, only the synthesis of BiVO4 electrodes, and not colloidal BiVO4 powders, has yielded materials with surface areas significantly higher than 10 m2 g-1.[34, 37, 38] Of note is that BiVO4 will sinter at temperatures higher than ca. 200 °C which limits additional processing of BiVO4 materials with features on the nanometer scale. The method used here was selected for the synthesis of crystalline monoclinic BiVO4 with high surface area which can be achieved at low temperature using a simple process. For comparison bulk BiVO4 was also prepared by mixing bismuth and vanadium precursors without a chelating agent.[35]

Visually, nan-BiVO4 and bulk BiVO4 appear as yellow powders. Scanning electron microscopy (SEM) (Fig. 1a) of nan-BiVO4 shows agglomerated particles with features that range in size from ca. 20 to 100 nm which are in contrast to the much larger m features for bulk BiVO4 (Fig. 1b). Powder X-ray diffraction (PXRD) data of nan-BiVO4 (Fig. 2) are consistent with crystalline monoclinic BiVO4 (JCPDS no. 14-0688), which was also observed for bulk BiVO4 (Fig. S2). The greater peak width for nan-BiVO4 indicate that nan-BiVO4 crystallites are smaller than those of bulk BiVO4 corroborating the SEM images. Using the Scherrer equation (ESI) gave an estimated crystallite size of 16 and 71 nm for nan- and bulk BiVO4, respectively. The surface area of nan-BiVO4 (7.9 m2 g-1) was determined by nitrogen adsorption (Fig. S1) which exhibited a type III isotherm typical of a non-porous material, and is much greater than the area determined for bulk BiVO4 (<0.1 m2 g-1).

Diffuse reflectance UV-vis spectroscopy (DRUVS) (Fig. 3) was used to estimate the band gaps of nan-BiVO4 and bulk BiVO4. The Kubelka-Munk function was applied to the reflectance data (Fig. S3) giving an estimated band-gap of 2.30 eV (540 nm) for nan-BiVO4 and 2.25 eV for bulk BiVO4 (550 nm), which is slightly lower than the reported band gap of monoclinic BiVO4 (2.4 eV, 520 nm).[34]



**Fig. 1.** SEM of a) nan-BiVO4 and b) bulk BiVO4.



**Fig. 2.** PXRD of nan-BiVO4. Indexing is consistent with the monoclinic polymorph (JSPDS no. 14-0688).



**Fig. 3.** DRUVS data for bulk BiVO4 and nan-BiVO4.

*3.2. Photocatalysis*

The photocatalytic activity of nan-BiVO4 was explored under visible light irradiation using a modified commercially available blue LED flood light (max = 470 nm) (Fig. S4). Initially the photooxidation of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde was examined. Previous reports of this reaction include the use of titanium dioxide irradiated by a visible light LED lamp[19] and bismuth tungstate[24], bismuth tungstate-reduced graphene oxide composites,[39] and bulk bismuth vanadate with an immobilised ruthenium photocatalyst[22], all irradiated under visible light using a 300 W Xe arc lamp. The bismuth tungstate-reduced graphene oxide composite appears to provide the state of the art, yielding full conversion of 0.1 mmol 4-methoxybenzyl alcohol in 6.5 h using 20 mg (ca. 0.04 mmol) of catalyst, but is a complex multicomponent system that requires several fabrication steps. Of the singular component photocatalysts, titanium dioxide requires 12.5 molar excess of catalyst irradiated for 4 h, and bismuth tungstate requires long irradiation times (22 h) from a Xe arc light source to give 4-methoxybenzyl alcohol conversion of ca. 95 %. It should be noted that rigorous comparison between photocatalytic systems is hampered by the different apparatus, catalysts concentrations and illumination sources.[40] Nevertheless, 0.1 mmol nan-BiVO4, without the aid of surface functionalised photocatalysts or additional components, is able to fully convert 0.1 mmol 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde selectively in 2.5 h using a blue LED (Table 1). Control experiments showed that at 40 °Cin the dark or in the absence of catalyst no conversion was observed, and in the absence of dioxygen, illumination for 4 h also gave no detectable conversion (Table S1).Therefore light, nan-BiVO4 and dioxygen are all required for reaction to occur confirming a photocatalytic reaction. Monitoring the reaction at 30 min intervals (Fig. 4) showed that the reaction appears to exhibit zero order kinetics at low conversion with a rate constant of 5.4 mmol dm-3 h-1. After ca. 80% conversion the rate deviates from linearity potentially a consequence of inhibition due to competitive adsorption (*vide infra*)

**Table 1**. Photocatalyst comparison between nan-BiVO4, bulk BiVO4 and P25 TiO2 for the photoxidation of 4-methoxybenzyl alcohol.



|  |  |  |  |
| --- | --- | --- | --- |
| Photocatalysta | Conversion (%)b | Selectivity (%)b | Yield (%)b |
| nan-BiVO4 | 97 | > 99 | 96 |
| bulk BiVO4 | 3 | > 99 | 3 |
| P25 TiO2 | 10 | > 99 | 10 |

a conditions: 0.1 mmol photocatalyst, 0.1 mmol 4-methoxybenzyl alcohol, 10 mL acetonitrile, 1 atm O2, blue LED irradiation for 2.5 h. bDetermined by 1H NMR (Fig. S6).



**Fig. 4.** The conversion of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde as a function of time. The 4-methoxybenzyl alcohol conversion and 4-methoxybenzaldehyde yield was determined using 1H NMR. The line for theoretical conversion of 4-methoxybenzaldehyde was derived from the zero-order rate constant.

Analogous experiments (Table 1) were performed using bulk BiVO4 and titanium dioxide (P25) for comparison with a literature system.19 After 3 h nan-BiVO4 exhibits ca. 30 and 10 times greater conversion in comparison to bulk BiVO4, and titania, respectively. Based on a band gap of (3.0 - 3.2 eV) titania is perhaps not expected to show activity under blue LED irradiation, however, visible light activity in TiO2 has been previously reported due to the creation of excitable states on alcohol adsorption.[19] However, low oxidation efficiency is observed which is confirmed in Table 1. nan-BiVO4 was also able to selectively oxidize a range of other benzyl alcohol derivatives to their corresponding aldehydes (Table 2).

In contrast to many photooxidation reactions, very little additional oxidation was observed, giving benzaldehyde selectivity > 90% in many cases. Conversions varied significantly between substituents. Electron donating groups such as methoxy and methyl gave very high conversions of > 99% and 97% respectively, whereas electron withdrawing groups such as nitro or trifluoromethyl substituents gave significantly lower conversions, of 46% and 48% respectively.

**Table 2**. The photo-oxidation of para-substituted benzyl alcohol derivatives to the corresponding aldehydes.

|  |  |  |  |
| --- | --- | --- | --- |
| R = | Conversion (%)a, b | Selectivity (%)a, b | Yield (%)a,b |
| Me | 97 | 90 | 87 |
| iPr | 75 | 91 | 68 |
| Ph | 58 | 88 | 51 |
| Cl | 66 | 94 | 62 |
| Br | 91 | 91 | 83 |
| I | 50 | 96 | 48 |
| CF3 | 48 | 83 | 39 |
| NO2 | 46 | 84 | 38 |
| C(O)OMe | 60 | 95 | 57 |
| NHC(O)Me | 87 | 100 | 86 |
| OMe | 100 | 100 | 98 |
| OH | 30 | 52 | 16 |
| H | 73 | 100 | 73 |

aconditions: 0.1 mmol photocatalyst, 0.1 mmol para-substituted benzyl alcohol, 10 mL acetonitrile, 1 atm O2, blue LED irradiation for 3 h. b Determined by 1H NMR (Fig. S6) except for R = H which was analysed by GC.

These data suggest that formation of an electron-poor intermediate controls activity and yield. An exception is the 4-hydroxybenzyl alcohol where a low conversion and selectivity of 30% and 52% respectively was found, presumably due to competitive chemistry between the two hydroxyl group moieties. Other work has also noted the reduced conversion of 4-hydroxybenzyl alcohol and selectivity for 4-hydroxybenzaldehyde which was attributed to competitive binding between the phenolic and benzylic OH groups.19

 Within the series R = Me, iPr and Ph, electronic factors cannot explain the conversions of 97, 75 and 58%, respectively, suggesting steric factors dominate. The trend suggests that larger substituents limit the number of alcohol molecules that can bind to the catalyst surface, although the footprint of each is expected to be similar. However, the precise mode of binding and local steric environment is unknown. Halogen substitution appears to show a balance of electronic and steric effects giving yields in the order I<Cl<Br, but again selectivity remains high for all. Repeats of the oxidation of 4-methoxybenzyl alcohol indicate that the reported percentage conversions given above have an error of +/- 5% (Table S2), indicating the trends in conversion associated to differing steric and electronic effects are significant.

 The data in Table 2 are in contrast to previous reports for single component visible light irradiated photocatalysts, where no significant steric or electronic substituent effects are evident. For example, Bi2WO6 results in ca. 55 % conversion for a range of different para substituted benzyl alcohols after 10 h of irradiation with a 300 W Xe arc lamp, fitted with 420 and 760 nm filters,[24] and ca. 90% conversion of a wide range of para-substituted benzyl alcohols after 4 h of irradiation, by a blue LED array (ca. 20 mW cm-2), has been achieved by a large excess of TiO2.[19] The use of a Bi2WO6-reduced graphene oxide composite[39] or a bulk BiVO4 loaded with a ruthenium photocatalyst[22] have shown that electron donating substituent groups result in higher benzyl alcohol conversions. However, it is difficult to draw mechanistic conclusions from these systems as the role of each component of these composite catalysts is unclear.

For derivatives resulting in lower conversion, the reaction time was extended (Table 3) and *i*Pr, I and Ph substituted benzyl alcohols, gave full conversion with no loss of selectivity. Interestingly, CF3 substitution exhibited very little change in conversion or selectivity on extended photolysis indicating the possibility of a reversible reaction, photostationary state, or catalyst poisoning. On irradiation of a reaction mixture with 4-(trifluoromethyl)benzaldehyde as substrate, no 4-(trifluoromethyl)benzyl alcohol was observed indicating that oxidation is irreversible and also the absence of a photostationary state. Therefore, the effects of product inhibition and catalytic poisoning from by-product formation were investigated.

**Table 3**. Oxidation of benzyl alcohols to corresponding aldehydes with extended irradiation times.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| R =  | Time/h | Conversion/%a, b | Selectivity/%a, b | Yield/%a, b |
| iPr | 8 | 100 | 94 | 93 |
| COOMe | 8 | 80 | 78 | 62 |
| NO2 | 12 | 74 | 77 | 57 |
| Cl | 12 | 95 | 87 | 82 |
| CF3 | 12 | 44 | 82 | 36 |
| OH | 22 | 36 | 65 | 23 |
| I | 24 | 100 | 90 | 89 |
| Ph | 24 | 100 | 97 | 96 |

aconditions: 0.1 mmol nan-BiVO4, 0.1 mmol para-substituted benzyl alcohol, 10 mL acetonitrile, 1 atm O2, blue LED irradiation. b Determined by 1H NMR (Fig. S6).

The effect of adding various quantities of aldehyde derivatives to the photocatalytic oxidation of 4-methoxybenzyl alcohol using nan-BiVO4 was studied in order to examine product inhibition (Fig. 5). Conversion of 4-methoxybenzyl alcohol reduces as the product aldehyde concentration is increased and no change in selectivity is observed. The effect of inhibition by other aldehydes was also investigated for the oxidation of 4-methoxybenzyl alcohol to probe electronic effects on reaction inhibition. Electron withdrawing 4-nitro and 4-trifluoromethyl benzaldehydes exhibit greater inhibition at low concentration, but at higher concentrations, 4-methoxybenzyl alcohol conversion is most significantly reduced by 4-methoxybenzaldehyde. On addition of 4 equivalents of 4-methoxybenzaldehyde conversion reduces from > 99 to 6%.



**Fig. 5.** The effect of para-substituted benzaldehyde addition to 4-methoxybenzyl alcohol oxidation reactions.

 Apart from direct inhibition by the aldehyde, the reduced conversion in Table 3 and Fig. 5 could potentially be explained by benzoic acids produced from additional photo-oxidation of the corresponding benzaldehyde. It is known that aldehyde selectivity from the oxidation of alcohols is difficult to achieve and over oxidation is common.[41, 42] Carboxylic acids are known to bind strongly to oxide surfaces and could block surface binding sites via strong H-bond adsorption or covalent bonding.[43] Indeed, peaks consistent with the presence of 4-methoxybenzoic acid were observed in the oxidation of 4-methoxybenzyl alcohol with 3 and 4 equivalents of 4-methoxybenzaldehyde added (1 and 2 mol% respectively) (Fig. S7). Evidence of benzoic acids was only observed in reactions with at least 3 equivalents of added aldehyde and other potential oxidation by-products such as benzoates and acetals[44] were not observed by NMR or GC. For other reactions, benzoic acid was not detected by NMR but could conceivably be retained at the nan-BiVO4 surface reducing conversion. Addition of 4-methoxybenzoic acid on the photocatalytic oxidation of 4-methoxybenzyl alcohol using nan-BiVO4 was investigated (Fig. 6).

 The addition of 1 mol% of 4-methoxybenzoic acid resulted in a reduction in 4-methoxybenzyl alcohol conversion of 50%. Importantly, this suggests that small amounts of over-oxidation of benzaldehydes to their corresponding benzoic acids results in strong benzoic acid binding to the catalyst surface which has a significant inhibition effect on further alcohol oxidation.

 To assess the reversibility of 4-methoxybenzoic acid binding to the surface of nan-BiVO4, 32.3 mg (0.1 mmol) nan-BiVO4 was stirred in a 10 mM solution of 4-methoxybenzoic acid in acetonitrile and repeatedly washed with acetonitrile. Subsequent use for photocatalytic aerobic oxidation of 4-methoxybenzyl alcohol gave 45% conversion indicating some irreversible addition of 4-methoxybenzoic acid to the surface of nan-BiVO4. However, alcohol conversion was still observed, showing that more than one type of catalytic site is capable of mediating oxidation.



**Fig. 6.** Addition of 4-methoxybenzoic acid to 4-methoxybenzyl alcohol oxidation. mol% is relative to 4-methoxybenzyl alcohol (0.1 mmol), 10 mL acetonitrile and 1 atm dioxygen used in each reaction.

Collectively the data suggest that small quantities of benzoic acids (products of over-oxidation) strongly inhibit photocatalytic oxidation of benzyl alcohols. Benzyl aldehydes (the main reaction products) may also contribute to the inhibition effect. Comparison of the conversion and selectivity data of Tables 2 and 3 indicate that product and by-product inhibition may be occurring. Whilst catalytic poisoning is a very common phenomenon in heterogeneous catalysis,[45-52] this is rarely considered for photocatalytic reactions, and the only related example is reported for the gas phase photooxidation of toluene using UV irradiated titania which showed that accumulated benzoic acid on the titania surface inhibits oxidation.[53]

Gas chromatography analysis of the oxidation of 4-nitrobenzyl alcohol and 4-(trifluoromethyl)benzyl alcohol showed only peaks attributable to alcohol, aldehyde and acid (Fig. S5) indicating that low selectivity for substrates including 4-nitrobenzyl-, and 4-(trifluoromethyl)benzyl alcohol (Table 2) results from losses during work-up likely arising from by-products that are volatile or adsorbed on the catalyst surface.

Catalyst recycling and stability were also investigated for photo-oxidation of 4-methoxybenzaldehyde over 4 cycles. Initial reaction gave essentially quantitative conversion and selectivity, but on recycling a reduction in conversion is observed (Fig. 7). The reason for the drop of conversion for the first reuse of the catalyst could be tentatively attributed to some irreversible binding of 4-methoxybenzoic acid (vide infra). Separation of nan-BiVO4 from the liquid results in some mechanical loss (ca. 10%) leading to some reduction in yield but overall nan-BiVO4 retains very similar reactivity over 4 subsequent reuses. Comparison of PXRD and SEM data before and after reaction indicated no observable change in structure or morphology.



**Fig. 7.** Recycling of nan-BiVO4 for the selective oxidation of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde.

*3.3. Mechanism*

Previous work has shown that C-H activation is a rate limiting step using TiO2 and carbon nitride, both irradiated by visible light, which show primary kinetic isotope effects of kH/kD = 3.9 and 3.3 respectively for PhCH2(OH)/PhCD2(OH) photooxidation.[19, 23] Using nan-BiVO4, reaction of PhCD2(OH) gave only PhC(O)D as judged by 1H and 2H NMR, and mass spectrometry, showing no exchange between either the precursor methylene moiety or product aldehyde proton, and the alcohol, aldehyde, residual water, or nan-BiVO4 surface hydroxyl moieties. Illumination for 1 h (49% conversion) of a 1:1 mixture of PhCH2(OH) and PhCD2(OH) gave kH/kD = 1.30. This is most consistent with a secondary isotope effect suggesting that C-H activation of the methylene group is not rate limiting in contrast to TiO2 and carbon nitride. A secondary isotope effect > 1 is consistent with a change in hybridisation in the rate determining step from an sp3 to sp2 carbon atom or conformational changes on surface binding.

 Steady state and time resolved photoluminescence spectroscopies were used to examine the photophysical properties and lifetimes of excited states that may be relevant to benzyl alcohol oxidation. The intensity of emission, and the lifetime of excited states, can be used to assess electron-hole recombination in irradiated semiconducting materials, which can be the limiting factor in photocatalysis. Measurements were also undertaken in the presence and absence of dioxygen and benzyl alcohol, to determine whether the lifetimes observed are associated to charge carriers that are chemically relevant to photocatalysis and help to distinguish between sites associated with recombination and/or catalysis. On excitation at 380 nm, the steady state photoluminescence spectrum for nan-BiVO4, (Fig. 8) shows two overlapping emission peaks at λ1max = 445 nm and λ2max = 475 nm. On addition of reagents emission is suppressed with a greater effect attributable to benzyl alcohol, presumably due to the lower solubility of O2 in acetonitrile.[54] The sensitivity of the emission peaks to benzoic acid and O2 suggests at least part of the intensity is attributable to surface states, which interact with the substrates. In comparison to nan-BiVO4, bulk BiVO4 exhibits significant less intensity which is consistent with fewer surface emission sites due to a lower surface area.

With respect to time resolved photoluminescence spectroscopy, reported data appears to be strongly sample dependent and assignment of emission bands is complicated by the various bulk and surface defect states that may be present dependent on the synthetic method.[55-61] Reported data for BiVO4 most often shows emission at ca. 470 - 550 nm, and is typically attributed generically to electron-hole recombination.[55, 56, 60] Related studies on BiVO4 using transient absorption spectroscopy have also been conducted over the picosecond to second timescales under electrical bias to inform photoelectrochemical water oxidation processes that chemically occur on the s to ms timescales.[62] Bands at 440 and 470 nm with lifetime components on the ns timescale have been assigned to electron-hole recombination between conduction band electrons and hole states above the valence band, and electron trapping between conduction band electrons and empty trap states below the conduction band, respectively[62].

Notwithstanding the specific assignment of the emission bands, the lifetimes of bulk and nan-BiVO4 in the absence of reagents (Table 4) show that bulk BiVO4 exhibits longer lifetimes than nan-BiVO4.The decay curves (Fig. S8) fit best to double exponentials (SI) with the magnitude of each contribution reflecting the amount of peak overlap for each transition at λ1max = 445 nm and λ2max = 475 nm, respectively. Table 4 shows data collected at the band edges of 420 and 500 nm which allows differentiation and assignment of the two time constants with the shorter ca. 3 ns component derived from λ1max = 445 nm and the longer ca. 10 ns component derived from λ2max = 475 nm. Experiments were also conducted in the presence of reactants for nan-BiVO4.Addition of benzoic acid and/or O2 to nan-BiVO4 reduces the lifetimes of both emission bands, where benzoic acid reduces the lifetime more significantly than O2,which is reflective of the steady state fluorescence data (Fig. 8).

 

**Fig. 8**. The steady state emission spectra for a 1 mg mL-1 dispersion of nan-BiVO4 in acetonitrile in the presence and absence of substrates from 400 to 700 nm, excitation wavelength 380 nm.

 The reagent dependent behaviour of the steady state and time resolved photoluminescence spectra strongly suggest that adsorption of the substrates occurs at sites also responsible for emission suggesting that these sites are also chemically relevant for oxidation of benzyl alcohol and reduction of oxygen, respectively.

**Table 4**. Excited state lifetimes of BiVO4 in acetonitrile

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Samplea | τ1/ns (A/%)b | τ2/ns (B/%)b | τ1/ns (A/%)c | τ2/ns (B/%)c |
| nan-BiVO4, N2  | 3.02±0.10 (56.2) | 10.86±0.47 (43.8) | 3.52±0.10 (45.1) | 11.91±0.37 (54.9)  |
| nan-BiVO4, O2  | 2.94±0.09(58.1) |  11.19±0.43 (41.9) | 3.45±0.11 (46.8) | 11.29±0.34 (53.2) |
| nan-BiVO4, N2, BnOH  | 2.25±0.04 (53.0) | 8.31±0.15 (47.0) | 3.41±0.10 (45.2) | 10.13±0.22 (54.8) |
| nan-BiVO4, O2, BnOH  | 2.29±0.06 (52.8) | 8.39±0.22 (47.2) | 3.08±0.09 (42.5) | 9.59±0.20 (57.5) |
| Bulk BiVO4, N2 | 3.63±0.27 (47.3) | 11.94±0.92 (52.7) | 4.18±0.34 (38.1) | 12.85±0.78 (61.9) |

a 1 mg mL-1 dispersion in MeCN, under 1 atm of N2 or O2, 0.1 mmol (10 mM) of benzyl alcohol (BnOH) bExcited state lifetime components (τn) and % contribution of components in brackets obtained from excitation at 380 nm and emission at 420 nm, cAnalogous data from excitation at 380 nm and emission at 500 nm.

 Collectively the results are consistent with the proposed mechanism in Scheme 1. Upon photon absorption, electron hole separation occurs with the carriers becoming trapped in surface defect states. Adsorption of substrates occurs at sites including those responsible for emissive recombination and the trapped electrons are transferred to surface adsorbed dioxygen, and holes to surface adsorbed benzyl alcohol molecules inducing reduction and oxidation respectively. Benzaldehyde is formed with liberation of protons that supports generation of water from the reduction of dioxygen derived species. Benzaldehyde can either desorb from the surface or be oxidised again to form benzoic acid, which can bind either reversibly or irreversibly and inhibit binding of alcohol substrate retarding reaction.



**Scheme 1** Proposed mechanism for the aerobic oxidation of benzyl alcohol with visible light irradiated nan-BiVO4.

**4 Conclusions**

Bismuth vanadate nanoparticles (nan-BiVO4) are selective heterogeneous photocatalysts for the oxidation of benzyl alcohols to benzaldehydes under blue LED irradiation. Structural characterisation, spectroscopic, and reactivity data suggest that whilst electron-hole recombination is more rapid for nan-BiVO4 than bulk BiVO4, the significant activity of nan-BiVO4 is supported by an increase in the number of sites that trap electrons and holes and adsorb substrates, due at least in part to an increase in surface area. Although for many substrates high conversions are found, inhibition by benzoic acid and to a lesser extent product benzaldehyde is observed suggesting competitive adsorption to the photocatalyst surface. This observation has an important general implication for selectivity and conversion in heterogeneous photocatalysis systems.

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