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Revisiting the Behaviour of BiVO₄ as a Carbon Dioxide Reduction Photo-Catalyst.

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Bismuth vanadate is a widely known photocatalyst for the hydro-reduction of CO2. In spite of the great appeal of such a catalytic system, problems arise due to deactivation of the catalyst with consequent low reaction yield. We have investigated the catalyst behavior during methanol production and have found that the catalyst irreversibly loses vanadium from the structure whilst depositing bismuth oxides on the surface of the catalyst. While catalyst activity can be restored upon heating, leaching of vanadium, leading in long term to catalyst decomposition, is unavoidable and irreversible.

Introduction

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The idea of using water as a hydrogenating agent for organic products, and for CO_2 in particular, is fascinating and potentially ground breaking. In 1978, Halmann M. was the first to report the photoelectrochemical reduction of CO2 in water using p-GaP¹, and ever since, a wide spectrum of semiconductors capable of both oxidizing water and reducing CO_2 is being actively pursued.^{2–5} The work of Bocarsly has marked a milestone in the production of light organic fuels from CO_2/H_2O mixtures, a process now referred to as "reverse combustion". To overcome the unfavourable thermodynamics of this highly desirable transformation energy has been provided with electro-,^{6,7} photo-^{8,9} or photo-electrochemical devices.^{10,11} However, the possibility of using purely photochemical devices remains the ultimate requisite for a completely sustainable and scalable reverse combustion.

Currently, titanium dioxide and BiVO₄ are the most popular photo-catalysts for this purpose. These materials have been modified to control size, conductivity and sensitivity to visible light 3,12-16. A plethora of other photo-semiconductors that can efficiently absorb visible light and convert CO₂ to light organic fuels, especially methanol and methane, has also been discovered $^{17\mathchar`-23}$. The unique popularity of $BiVO_4$ is justified by its demonstrated versatility as a water oxidation catalyst for alcohol production from CO₂ and selective also photodegradation of organic waste^{24–27}. Monoclinic BiVO₄ has conduction and valence bands which are well suited for water oxidation coupled with CO₂ reduction and hydrogen evolution (Figure 1). Its usage is in principle advantageous over other common water oxidation catalysts, including TiO₂, due to its narrow band gap of ~2.4 eV, which allows ready absorption of visible light.

Furthermore, BiVO₄ has also been demonstrated versatile photosemiconductor for the reduction of CO₂ into methanol and ethanol^{22,23}. The authors of these remarkable findings have reported promising hydrocarbon yields along with the possibility of regenerating BiVO₄ upon heating. The ability of regenerating BiVO₄ is a critical point for the performance of this photosemiconductor and which remains otherwise regrettably limited. In addition, BiVO₄ has been deposited over anodes to photo-electroanodes of improved prepare catalytic behaviour.²⁸ A recent study, however, has clearly demonstrated the corrosion of the BiVO₄ film of the photo-anode in alkali medium thus reiterating the previously suspected ability of this binary oxide to irreversibly leach vanadium in alkali solution²⁹.

This led us now to reconsider the activation/deactivation paths of BiVO₄ in purely photochemical processes and not involving electrochemical input²⁹ which might otherwise decrease the stability of BiVO₄ by accelerating the loss of vanadium.



Figure 1. Band structure of monoclinic BiVO4 and anatase TiO2 demonstrating filled valence bands on the bottom (more positive) and empty conduction bands at the top (more negative) ^{30,31}.

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Experimental

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Synthesis of Semiconductors

Synthesis of *m***-BiVO**₄ **hyperbranched crystals:** Monoclinic BiVO₄ was prepared by a CTAB-assisted hydrothermal method as reported by Liu et al.²²

Synthesis of *m*-BiVO₄ polyhedral crystals: Bi(NO₃)₃.5H₂O, NH₄VO₃ and Na₂SO₄ were added to water in a molar ratio 1:1:1.1, respectively. The mixture was stirred in a glass vessel pressure vessel forming a yellow solid and heated to 180°C for 24h. The solid was filtered and washed with three portions of cold water. The solid was dried at 140°C for 12h. The resulting solid was analysed by powder X-ray diffraction (XRD) and was in agreement with published monoclinic bismuth vanadate.

Catalytic Testing

In a typical reaction, 0.4 g of catalyst and 200 mL of a 1.0 M NaOH solution were place in a quartz flat bottom flask adjacent to a 300 W Xe arc-lamp. Prior to light irradiation, the reaction mixture was thoroughly degassed and allowed to equilibrate under a CO₂ atmosphere for 30 minutes. Methanol was detected with an Agilent 7820A GC with a flame ionization detector (FID), using a Restek Rt-U-Bond column and helium carrier gas. ⁵¹V NMR spectra were recorded on a Bruker Avance II 300 MHz spectrometer using neat VOCl₃ as a standard. Chemical shifts are reported in p.p.m. Spectra were recorded at 298 K. Powder XRD diffractograms were obtained on a Rigaku diffractometer. X-ray Fluorescence Ultima IV (XRF) measurements were performed on a Rigaku Supermini-200. UV-Vis spectra were obtained on a Specmate UV-1100 spectrometer. Scanning electron microscopy and energy dispersive X-ray analysis was performed with a JSM-7500F SEM instrument by JEOL, Inc. The concentration of formaldehyde was determined by a colorimetric procedure by Nash³². Concentration of dissolved formate was determined by a colorimetric procedure by Sleat and Mah.³³

Results and Discussion

CO₂ reduction

In this study, we focused on using hyperbranched structures (hyp-BiVO₄) for CO₂ reduction due to high activity, and for decomposition studies both polyhedral crystals (poly-BiVO₄) and hyperbranched structures (hyp-BiVO₄) (Figure 2).

Both hyp-BiVO₄ and poly-BiVO₄ are capable of reducing carbon dioxide into methanol. Literature data indicate that the methanol production reaches a maximum with no decomposition¹⁴.



Figure 2. a) Polyhedral crystals of monoclinic BiVO4 and b) hyperbranched crystals of monoclinic BiVO4.

Similarly, it has previously been shown that the BiWQALCED, be reactivated simply by heating the catalyst 8080 c9 with Pittle 1658 of activity ²³. In all of our experiments, we saw both a decrease in methanol concentration after 200 minutes of catalytic testing and a permanent deactivation of the catalyst after reactivation by heating. This is in contrast to other published work,²³ where a linear production of methanol was observed with little loss of activity after regeneration. In an attempt to understand these discrepancies, further investigation of the intermediate products and catalyst composition were performed with pristine and reactivated BiVO4.



Figure 3. Concentration of a) methanol, b) formaldehyde and c) formate during catalysis.

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Table 1. Quantitative analysis of oxidation and reduction of intermediates and products with BiVO4 after 24 hr.

Starting	MeOH	CH ₂ O	HCOO-	H ₂
Material	(µmol)	(µmol)	(µmol)	(µmol)
Methanol		28	13	3.6
Formaldehyde	460		71	25
Sodium	300	n.d.		n.d.
formate				

While we did not observe the formation of EtOH as reported in the literature,²² both formate anion and formaldehyde, along with methylformate were generated during the catalytic runs. Formate concentration appears to stabilize after 3 hours without loss of activity. Formaldehyde and methanol production decreases after recovery of the BiVO₄ catalyst, although the activity in formate formation does not appear to be affected by catalyst recovery. In all cases, no methane was detected confirming that the methanol loss after initial formation (Figure 3a) is not due to further reduction. We attribute the loss of methanol to the re-oxidation into lower value organics, including formaldehyde and formate by either BiVO₄ or the quartz reactor. The oxidation of several alcohols, including methanol into formaldehyde, has been shown to occur in glass and quartz reaction vessels upon irradiation³⁴. No other small organic molecules were detected. This perhaps could be taken as evidence for CO₂ photoreduction to initiate via monodentate binding, with stepwise proton-coupled electron transfers producing methanol as a final product.

Potential oxidation products of methanol, formaldehyde, and sodium formate (Table 1) in a 1M solution of NaOH were studied to help decipher the pathway for methanol reoxidation. In all cases methane, carbon monoxide or other organic products were not observed.

To observe the effect of formaldehyde on $BiVO_4$, an experiment was performed with formaldehyde as the starting organic material. Interestingly, when this $BiVO_4$ catalyst was analysed by XRD and SEM, large amounts of $Bi2O_{4-x}$ nanoparticles were detected over the starting $BiVO_4$ (Figure 5).



Figure 5. Comparison of powder XRD patterns of A) inactive hyp-BiVO4 from reaction with formaldehyde B) inactive hyp-BiVO4 from CO2 photoreduction and C) literature spectrum of Bi_2O_{4-x} . SEM micrograph of hyp-BiVO4 from formaldehyde-spiked conditions is inset

This effect is also seen during methanol production but to a lesser extent. The heavy coating of the active surface of $BiVO_4$, which is present only in inactive samples, suggests that this coating is at least partially responsible for the deactivation of the catalyst. This likely occurs due to blocking of the active surface by the coating of bismuth oxide, which can be partially removed by regenerating the catalyst during heating.

From the experiments of BiVO₄ with formaldehyde, we observe that the deposition of $Bi2O_{4-x}$ is caused at the surface of the catalyst by a reaction with formaldehyde, one of the key intermediates in the reduction to methanol. In turn, this indicated irreversible loss of vanadium from the original BiVO₄ structure.

Several unsuccessful attempts were performed to try to reinsert the vanadium back into the etched BiVO₄ structures by illuminating with various vanadium sources in water (NH₄VO₃ or etched vanadium solution).



Figure 4. SEM images of (a) pristine, (b) inactive, and c) reactivated poly-BiVO4, and (d) pristine, (e) inactive and (f) reactivated hyp-BiVO4.

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Catalyst deactivation

The activity of BiVO₄ towards CO₂ photoreduction necessarily requires the use of base ²². However we have found that in 1M NaOH aqueous solutions, both with and without 1 atmosphere of CO₂, BiVO₄ will become etched and Bi₂O_{4-x} nanoparticles are deposited on the surface of the catalyst (Figure 4 b/e). By using a backscatter filter to determine surface electron density, deposited nanoparticles are revealed to be very dense, compared to bulk BiVO₄. In this state, the catalyst has become deactivated and shows limited CO2 reduction activity. The etching has also been shown to occur without illumination³⁵. The catalyst can be reactivated by heating to 150°C which removes the electron rich deposits from the surface by drawing vanadium density from the inner BiVO₄. Although the catalyst can be reactivated, it remains irreversibly etched (Figure 4 c/f). The reactivated catalyst was tested for CO₂ reduction under the same conditions and was shown to have reduced activity compared to pristine BiVO₄ (Figure 3). Composition of the BiVO₄ surface was analysed during all stages of BiVO₄ regeneration (Table 2).

Table 2. Energy dispersive spectroscopy (EDS) derived molar % of bismuth, vanadium and oxygen on the surface of hyp-BiVO4 averaged over three samples.

Sample	% Bi	% V	% O
Pristine hyp-	$\textbf{15.3} \pm \textbf{1.4}$	15.2 ± 1.5	69.5 ± 2.7
BiVO ₄			
Inactive hyp-	17.6 ±0.7	13.52 ± 0.4	69.4 ± 1.1
BiVO ₄			
Reactivated	16.7 ±0.3	13.92 ± 0.02	$68.8\pm\!\!0.4$
hyp-BiVO₄			
Dried hyp-BiVO ₄	0.00	19.0 ±2.4	81.0 ±2.4
filtrate			

XRD data (Figure 7) reveals the formation of a new crystalling material contaminating the sample of BiVO2. The contamination peaks correspond with literature samples of a mixed valence bismuth oxide, denoted as $Bi_2O_{4-x}^{36}$. Attempts to separate this contaminant from the bulk BiVO4 have been unsuccessful. We assign the electron rich surface deposits (Figure 6) to Bi_2O_{4-x} .

The molar percent of oxygen does not change significantly between samples (Table 2), although vanadium and bismuth percentages are greatly altered in post-reaction. Pristine hyp-BiVO₄ has a ratio of 0.99 V/Bi, by surface molar percentage. This is compared to the inactive ratio of 0.77 and the recovered ratio of 0.83. This confirms that a large amount of surface vanadium is irreversibly lost during the reaction, likely caused by leaching in the alkaline conditions. Similar losses of vanadium were observed from the structure by XRF measurements (see S.I.). To confirm that vanadium was lost to the filtrate, a sample of the filtrate was dried and EDS measurements of the filtrate taken which shows only vanadium in solution (Figure 6b). This is further confirmed by ⁵¹V NMR of the filtrate which shows multiple peaks, characteristic of a mixture of aqueous vanadium oxides (Figure 4c).

In addition to visual modifications and vanadium leaching, the bulk inactive catalyst undergoes changes in its crystal structure (Figure 7).



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Figure 7. Powder X-ray Diffraction (XRD) patterns of (A) Literature pattern of Bi2O4-x. (B) pristine hyp-BiVO4, (C) inactive hyp-BiVO4 and (D) reactivated hyp-BiVO4.

Conclusions

This work has provided a new insight into the decay mechanism of $BiVO_4$ as a photocatalyst for CO_2 photoreduction. A major deactivation pathway appears to be caused by the reoxidation of its own products. In this case, even as the catalyst activity is improved (by improving charge separation, decreasing recombination rates, etc.) $BiVO_4$ will rapidly decay with loss of vanadium and deposition of bismuth oxides and will require constant recovery by heating. However, vanadium leaching and catalyst etching are irreversible processes, and after every catalytic cycle of photoreduction/recovery, a portion of the initial catalyst will be lost.



Figure 8. Schematic of pristine ${\rm BiVO_4},$ deactivated ${\rm BiVO_4}$ and reactivated ${\rm BiVO_4}$

The major and minor products formed in this reaction provide insight into the mechanism of CO_2 photoreduction for BiVO₄. While formaldehyde, formate and methanol are all possible products in all three proposed CO_2 reduction pathways, the lack of other key intermediates detected (CO, glyoxal, etc.) suggests the formaldehyde pathway is the most likely pathway for CO_2 reduction, at least when catalyzed by BiVO₄.

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The acknowledgements come at the end of an article after the conclusions and before the notes and references.

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