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Short Communication

Chemoselective and highly efficient conversion of aromatic alcohols into aldehydes photo-catalyzed by Ag₃PO₄ in aqueous suspension under simulated sunlight



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ABSTRACT

Achieving alcohol to aldehyde conversion in an energy efficient and environmentally benign way still remains a challenge. Here, we report chemoselective (>99%) and efficient conversion (>90%) of alcohols to corresponding aldehydes photocatalyzed by Ag_3PO_4 in water at room temperature under simulated sunlight excitation. A plausible mechanism for the observed high selectivity is proposed. The mechanism suggested that the reduction site of the semiconductor photocatalysts is more critical to be engineered in order to obtain high chemoselectivity in case of alcohol oxidation.

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1. Introduction

Ever since the discovery of light-activated water splitting on a TiO₂ electrode (the so-called Honda effect) [1], photocatalytic processes have been widely investigated owing to their renewable attributes. Most of the earlier studies involving photocatalysis focused on environmental cleanup, H₂ production, and CO₂ reduction etc. [2–4]. Recently, the utilization of the photocatalytic process for the synthesis of fine chemicals via an environmentally benign pathway has been explored [5–7]. Attempts have been made to achieve numerous functional group transformations, such as amine to imine [8,9], nitro to azo [10], aniline to azobenzene [11], hexane to hexanone and hexanol [12], and alcohols to corresponding aldehydes, [13-17] among others. The last one being one of the most important organic synthesis as aldehydes are widely used in food, beverages, pharmaceutical industries and as precursors in chemical industries [18,19]. In the conventional alcohol oxidation approaches, many advances have been made where metalbased selective and efficient oxidization reagents have evolved, but the requirement of stoichiometric amounts of the metal oxidants and accumulation of a considerable amount of waste is inevitable [18,20].

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On the contrary, semiconductor-mediated photocatalytic process in context of selective oxidation is still in its infancy as new photocatalysts are being explored to achieve oxidation of alcohols in a green fashion. Some of the photocatalysts investigated for alcohol oxidation include CdS/graphene [21] and CdS/graphene/TiO₂ [22]. Although selective and complete oxidation of benzyl alcohol to benzaldehyde was achieved in aqueous suspensions of Au/CeO₂, the reaction rate was rather low for the benzaldehyde formation (3.0 μ molh⁻¹) [23,24]. Pristine (rutile [13,15], anatase [17], and brookite [25]) as well as surface-modified titania (Nb₂O₅/TiO₂ [26], Pt/TiO₂ [27], transition metals/TiO₂ [28]) were investigated and it was notably discerned that the rutile form was the most selective oxidation photocatalyst [13]. Recently, chemoselective oxidation of alcohols was achieved using monolayer HNb₃O₈ 2D nanosheets under visible light irradiation [29]. In most of the previous studies, organic solvents were used to achieve high selectivity.

One of the intrinsic prerequisites of the photocatalysts for high selectivity and conversion appears to be a combination of high oxidation potential of valence band holes and low reduction potential of conduction band electrons. Recently, silver orthophosphate (Ag₃PO₄) is reported to have exceptional before-mentioned electronic attributes [30,31]. Herein, we report Ag₃PO₄-mediated selective, efficient and complete conversion of some representative alcohols (benzyl alcohol (BA), 4-methoxy benzyl alcohol (4-MBA) and cinnamyl alcohol (CA) to the corresponding aldehydes with high yield in aqueous suspensions under simulated sunlight excitation at room temperature.



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2. Experimental section

 Ag_3PO_4 was prepared following the synthesis procedure documented in the literature.^{19a} In a typical synthesis, a required amount of $Na_2HPO_4.7H_2O$ (0.27 g, 0.001 mol) was dissolved in double distilled water (50 ml) followed by addition of $AgNO_3$ (0.34 g, 0.002 mol). A bright yellow precipitate was immediately formed and the resulting suspension was kept under stirring for 2 h for a complete reaction. The product was collected by centrifugation, washed several times with water and ethanol and was dried at 90 °C for overnight. Details of characterizations, photocatalytic reactions, GC-MS analysis, photoluminescence studies and *in situ* ATR-FTIR study have been provided in supplementary information.

3. Results and discussion

Fig. 1 shows scanning microscopic image and XRD pattern of Ag_3PO_4 . The particle agglomerates have sharp-faceted features of fractured surfaces and fall in the range of ~0.5 to 2 µm. The XRD analysis revealed the formation of a single phase crystalline material and the peaks could be indexed as those belonging to Ag_3PO_4 in the BCC structure (JCPDS no.: 6-505); the sharpness of the peaks is representative of a polycrystalline material. Optical properties were examined by diffuse reflectance spectroscopy, Fig. 1(c) & (d), which evinced that Ag_3PO_4 is capable of absorbing light with wavelengths shorter than 530 nm. Direct and indirect band gaps were measured to be 2.42 and 2.34 eV, respectively.

To evaluate the activity and selectivity of Ag₃PO₄, the oxidation reactions were carried out in water at room temperature and ambient pressure using a light source that simulated sunlight. The conversion of BA to benzaldehyde was followed by GC-MS analysis and the complete course of evolution in BA and benzaldehyde concentration with irradiation time is presented in Fig. S2. In addition, analysis of irradiated samples taken out at regular time interval was carried out by UPLC to substantiate the GC-MS analysis. An exemplified time-dependent conversion of benzyl alcohol to benzaldehyde is shown in Fig. 2. As can be seen, ~90% of BA was converted to benzaldehyde with ~90% yield after ~4 h of irradiation. A quantitative analysis of BA and benzaldehyde concentrations revealed the mole-to-mole conversion. In order to assess the performance and selectivity of Ag₃PO₄ for other alcohols, oxidation of 4-MBA and cinnamyl alcohol was also studied. The results are summarized in Table 1 and compared with some significant studies documented in the literature focusing on the selective photocatalytic oxidation of alcohols. As was the case with BA, 4-MBA also underwent >85% oxidation forming anisaldehyde with selectivity exceeding 99% (on mole-to-mole conversion basis). However, in the case of cinnamyl alcohol, although the conversion was ~90%, selectivity was partially lost as benzaldehyde and benzene acetaldehyde were also formed in addition to cinnamaldehyde, whose yield was ~81%. Time-dependent conversion of 4-methoxybenzyl alcohol into p-anisaldehyde and cinnamyl alcohol into cinnamaldehyde is shown in Fig. 2(b) and (c), respectively.

Although one of the overriding limitations in achieving selective oxidation by the photocatalytic process is the overoxidation of reactants or products during longer irradiation time, no change in aldehyde concentration occurred even after 8 h signifying that the Ag₃PO₄ was extremely selective for BA, but not for benzaldehyde oxidation. In a recent study [32], the overoxidation or simultaneous oxidation of benzyl alcohol and benzaldehyde has been attributed to the complexation of benzaldehydes, unlike benzyl alcohol, with the TiO₂ surface. Interestingly, the overoxidation was much averted when the TiO₂ surface was substantially covered with the layers of WO₃ as WO₃ was found to be passive towards surface complexation with benzaldehyde. In this study, to investigate if there is any interaction between BA or benzaldehyde and Ag₃PO₄ surface, adsorption experiments were carried out by



Fig. 1. (a) Field emission scanning electron microscopic image, (b) powder XRD patterns, and (c) & (d) diffuse reflectance of Ag₃PO₄.



Fig. 2. Change in the concentrations of (a) benzyl alcohol, (b) 4-methoxybenzyl alcohol and (c) cinnamyl alcohol into corresponding aldehydes upon irradiation. Experimental conditions: $Ag_3PO_4 = 2 gl^{-1}$, initial alcohol concentration = 0.6 mM, irradiation time = 8 h, and volume (H_2O) = 130 ml.

stirring the aqueous suspension of Ag₃PO₄ with BA or aldehyde or mixture of BA and benzaldehyde (1:1 volume ratio) under dark for 24 h. After experiment, the catalyst was separated by centrifugation and dried under vacuum, and the change in catalyst's surface was followed by FTIR & Raman, while any change in alcohol or aldehyde concentration was analyzed by GC-MS. The presence of any trace of alcohol or aldehyde was not noticeable, as could be seen from FTIR spectrums illustrated in Fig. S3. Furthermore, GC-MS analysis did not indicate any apparent change in alcohol or aldehyde concentrations. The dearth of noticeable physisorption of BA or benzaldehyde onto the surface of Ag₃PO₄ explains, to a certain extent, the suppression of aldehyde oxidation. Furthermore, controlled experiments, in the absence of catalyst or

Table 1

A comparative oxidation of selected aromatic alcohols by heterogeneous photocatalytic process.

Catalyst	Substrate	Product	Conversion (%)	Selectivity (%)	Yield (%)	Conditions	Reference
TiO ₂	BA	Benzaldehvde	50	38	(*)	H ₂ O, UV light	[13.14]
- <u>2</u>	4-MBA	p-Anisaldehyde	50	60	(*)	2.,, 0	
TiO ₂	BA	Benzaldehyde	42	95	(*)	Trifluorotoluene, UV light	[16]
SiO ₂ /TiO ₂	BA	Benzaldehyde	46	95	(*)		
SiO_2/TiO_2 (modified with H ₂ SO ₄)	BA	Benzaldehyde	90	95	(*)		
TiO ₂	4-MBA	p-Anisaldehyde	65	(*)	41.5	H ₂ O, UV light	[17]
CdS/graphene	BA	Benzaldehyde	45	90	45	Trifluorotoluene, visible light	[21]
CdS/graphene/TiO ₂	BA	Benzaldehyde	>80	>90	<80	Trifluorotoluene, visible light	[22]
Au/CeO ₂	BA	Benzaldehyde	>99	>99	>99	H ₂ O, visible light	[23,24]
TiO ₂	4-MBA	p-Anisaldehyde	50	56	(*)	H ₂ O, UV light	[25]
Pt/TiO ₂	BA	Benzaldehyde	87	68	(*)	H ₂ O, visible light	[27]
	4-MBA	p-Anisaldehyde	85	90	(*)		
	Cinnamyl alcohol	Cinnamaldehyde	95	71	(*)		
Ir/TiO ₂	BA	Benzaldehyde	~9	92	(*)	H ₂ O, UV light	[28]
HNb ₃ O ₈	BA	Benzaldehyde	20	>99	(*)	Benzotrifluoride, visible light	[29]
	4-MBA	p-Anisaldehyde	63	85	(*)		
WO ₃ /TiO ₂	BA	Benzaldehyde	50	56	(*)	H_2O , light >350 nm	[32]
Ag ₃ PO ₄	BA	Benzaldehyde	>85	>99	~85	H ₂ O, simulated sunlight	[in this study]
	4-MBA	p-Anisaldehyde	>85	>99	~85		
	Cinnamyl alcohol	Cinnamaldehyde	~90	>90(**)	~81		

(*) not mentioned, (**) traces of benzaldehyde and benzene acetaldehyde were also formed. BA-benzyl alcohol; 4-MBA-4-methoxy benzyl alcohol.



Fig. 3. Change in selected ATR-FTIR spectra of BA with time in the presence of Ag₃PO₄ (a) under light and (b) under dark.

light, were also performed which did not show any change in alcohol concentration, indicating that both light and catalyst were required to trigger and sustain the oxidation.

The course of BA oxidation was also pursued by an *in situ* ATR-FTIR analysis and this study was carried out in conditions analogous to photocatalytic conditions. A time-dependent evolution in ATR-FTIR spectra in the presence of Ag_3PO_4 under light and darkness is presented in Fig. 3. The spectrums of BA and benzaldehyde solution prepared in water were also recorded and included in Fig. 3 for comparison. Aldehyde C–H stretches at ~2700 and 2800 cm⁻¹ were not observed. Under the light, the intensity of absorption bands at 1655 cm⁻¹ was decreased while the intensity of bands at 924, 1004, 1023, 1206, 1393 and 1456 cm⁻¹ was found to increase with increasing irradiation time. Few new absorption bands appeared at 826, 1012, 1585 and 1599 cm⁻¹.

Absorption bands of BA modified gradually with respect to irradiation time and started to resemble that of benzaldehyde. Notably, the absorption band corresponding to the carbonyl (C=O) stretching vibration, which essentially differentiate BA and benzaldehyde, apparently appeared at ~1697 cm⁻¹. This band appeared after 20 min of irradiation and the intensity was steadily increased with irradiation time. Whereas under dark, with or without Ag₃PO₄, it did not appear even after 120 min of irradiation corroborating our earlier observation that light and Ag₃PO₄ were necessary to instigate the oxidation of BA.

Unlike previous reports on the photocatalytic oxidation of alcohols as presented in Table 1, greater selectivity was observed in this study. Essentially, the non-selective nature of photocatalysis could be attributed to the formation of extremely reactive and short-lived radicals such as OH^* , O_2^{-*} , HO_2 etc. O_2 is readily reduced to O_2^{-*} by excited conduction



Scheme 1. A probable mechanism of photocatalytic oxidation of BA.



Fig. 4. XRD patterns of Ag_3PO_4 collected after different irradiation time showing the formation of metallic Ag. Ag^{**} -metallic Ag collected after dissolving the mixture of Ag and Ag_3PO_4 obtained after irradiation experiments.

band electrons while the holes in the valence band can oxidize water, generating OH[•] radicals. These radical species are extremely reactive, though short lived, and make the photocatalytic process somewhat non-selective. Particularly, O₂ may affect the overall photocatalytic oxidation in two ways; as an oxidant (electron acceptor) or direct incorporation of molecular oxygen to yield a product. Hence, formation or the involvement of such radicals was examined in order to understand the operative mechanism responsible for the high selectivity. To determine the role of O_2^{-1} , the oxidation of BA was carried out both in the absence and presence of molecular O₂, by bubbling N₂ or O₂ through photoreactor. Results showed that the conversion was independent of the ambient environment, indicating that O₂ seemingly did not play any role in the oxidation of BA. This could be attributed to the lower or more negative redox potential of $O_2/O_2 - \bullet (-0.16 \text{ eV}, 1 \text{ M vs. NHE})$ at pH = 7 [33,34]) than the electrode potential of Ag_3PO_4 (+0.8 eV vs. NHE at pH = 7) [30]. The findings further suggested that the oxidation of alcohols via the photocatalytic process essentially proceeds through the involvement of valence band holes, rather than direct incorporation of molecular oxygen. Based on these observations, a plausible mechanism involving 2 electrons and protons transfer process that operates in the oxidation of alcohols to corresponding aldehydes is illustrated in Scheme 1. Furthermore, the path A appears to be more likely as the formation of radical at the β -carbon may result in the delocalization of this electron in the adjacent benzene ring, imparting additional stability and rather thermodynamically favorable oxidation of BA. It seemed plausible to postulate that the excited electrons were taken up by Ag^+ ions of the Ag_3PO_4 because the standard redox potential of



Scheme 2. Schematic showing involvement of O_2^{-*} , OH^{*} and holes in the selective photocatalytic oxidation of alcohols. R = aryl group.

Ag (I) $(Ag^+/Ag^0 = +0.8 \text{ eV})$ is higher or more positive than the conduction band potential of Ag_3PO_4 which implies that the Ag^+ is likely to be reduced to Ag⁰ by excited conduction band electrons. This assumption was corroborated by XRD analysis of irradiated/used Ag₃PO₄, which showed the presence of metallic silver in the sample. Change in the structure of Ag₃PO₄ or appearance of metallic silver with respect to irradiation time was followed by XRD and obtained diffraction patterns are presented in Fig. 4. In addition to characteristic diffraction peaks of Ag₃PO₄ which indicated the retention of basic Ag₃PO₄ structure, 4 new peaks (indicated with "*") appeared which can be indexed as the (111), (200), (220) and (311) planes of metallic silver (JCPDS No. 04-0783). Moreover, formation of metallic silver with respect to irradiation time was also analyzed quantitatively by gravimetric analysis and the obtained values are listed in Table S1. As could be seen, the amount of Ag⁰ increases with the increase in irradiation time. For comparison, typical XRD diffraction patterns of Ag collected after irradiation reaction have been presented in Fig. 4. The patterns confirmed that the collected Ag was metallic and pure (free from silver phosphate).

Additionally, the role of OH[•] produced through water oxidation in the reaction media was investigated. Since terephthalic acid tends to trap OH[•] radicals and gets transformed into fluorescent 2hydroxyterephthalic [35], photocatalytic experiments were performed to monitor the generation of OH[•] via employing terephthalic acid as a probe molecule both in the absence or presence of BA. The change in fluorescence intensity, which is a function of OH radicals, was monitored by photoluminescence. The time-dependent evolution of the



Fig. 5. Change in fluorescence intensity of terephthalic acid with respect to irradiation time in aqueous suspensions of Ag₃PO₄ in (a) the absence or (b) the presence of BA.



Fig. 6. Effect of Ag₃PO₄ recycling on the formation of benzaldehyde from benzyl alcohol. Experimental conditions: Ag₃PO₄ = 2 gl⁻¹, initial alcohol concentration = 0.6 mM, irradiation time = 4 h, and volume (H₂O) = 130 ml.

fluorescence spectra for terephthalic or 2-hydroxyterephthalic acid in the absence or presence of BA is shown in Fig. 5. High intensity was observed when terephthalic acid was irradiated without BA, indicating generation of OH^{*} via oxidation of H₂O. However, in the presence of BA, the intensity was strongly suppressed revealing preferred oxidation of BA over that of water. The observed role of O₂, accompanied by Ag⁺ to Ag⁰ reduction and suppression of OH^{*} formation, corroborates the plausible mechanism depicted in Scheme 2 for the selective oxidation of alcohols in the presence of Ag₃PO₄.

The recyclability of Ag_3PO_4 was investigated under the identical experimental conditions as applied for the study of photocatalytic oxidation of BA. After the completion of the reaction (each cycle), the catalyst was collected by centrifugation, washed with water and ethanol, dried at 90 °C and was utilized for the next cycle. The effect of recyclability on the formation of benzaldehyde is shown in Fig. 6. As could be seen, the benzaldehyde formation was decreased by ~12%, 28% and 48% for the cycles first, second and third, respectively. The decrease in the photocatalytic efficiency of Ag_3PO_4 may be explained in terms of silver reduction ($Ag^{+1}-Ag^0$) by the excited electrons during photocatalytic processes, as discussed above and presented in Scheme 2. As the irradiation/exposure time of Ag_3PO_4 increases, more and more silver are likely to undergo photoreduction and thus leading to the decrease in the photocatalytic efficiency of the catalyst after every cycle.

4. Conclusions

We have demonstrated that selective and efficient photo-conversion of alcohols into corresponding aldehydes with high yield could be achieved with Ag_3PO_4 in water under mild conditions. Enhanced activity and selectivity are attributed to the high oxidation potential of Ag_3PO_4 , passive behavior of O_2^- , and weak generation and ineffectiveness of OH⁺ radicals. It seems likely that the valence band holes are the primary catalytic sites for the oxidation of alcohols, rather than direct oxidation through molecular oxygen, and chemoselectivity hinges on the engineering of reduction site or conduction band of the photocatalyst. Mechanistic observations may be anticipated to offer impetus to identify or custom-tailor other potential photocatalysts for selective photocatalytic oxidations. Although oxidation of few selected alcohols only was demonstrated, Ag_3PO_4 is likely to be active for a variety of other essential oxidation reactions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2014.08.025. These data include MOL files and InChiKeys of the most important compounds described in this article.

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