

# Zirconia-supported sodium decatungstate ( $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$ ): An efficient, green and recyclable photocatalyst for selective oxidation of activated alcohols to carbonyl compounds with $\text{O}_2$

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## Abstract

Zirconia-supported sodium decatungstate,  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$ , was prepared by incorporating  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  cluster into zirconia matrix via a sol–gel technique and used as a green and recyclable heterogeneous photocatalyst for oxidation of a variety of benzylic alcohols with  $\text{O}_2$  in  $\text{CH}_3\text{CN}$  which resulted in the corresponding aldehydes and ketones selectively in moderate to excellent yields. High inter- and intra-molecular chemoselectivities were observed when benzylic OH groups were oxidized in the presence of aliphatic OH groups. Non-benzylic alcohols were less reactive under the conditions established here. The photocatalyst has been reused several times, without observable loss of activity and selectivity. Heterogeneous photocatalyst is more active than the unsupported  $\text{Na}_4\text{W}_{10}\text{O}_{32}$ .

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**Keywords:** Benzylic alcohols; Photocatalyst; Oxidation; Sol–gel technique; Zirconia-supported; Sodium decatungstate

## 1. Introduction

The photoredox chemistry of polyoxotungstates (POTs) such as  $\text{W}_7\text{O}_{24}^{6-}$ ,  $\text{W}_{10}\text{O}_{32}^{4-}$ ,  $\text{PW}_{12}\text{O}_{40}^{3-}$ ,  $\text{SiW}_{12}\text{O}_{40}^{4-}$  and  $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$  in the presence of organic compounds, which resulted in reduction of the former and oxidation of the latter, have been extensively studied [1,2]. It is well known that the photocatalytic efficiency of POTs is comparable to that of the semiconductor  $\text{TiO}_2$  [3,4]. The outstanding photocatalytic ability of these non-toxic and green compounds is attributed to the existence of the  $\text{O} \rightarrow \text{W LMCT}$  band in their UV–vis absorption spectrum. Hence, illumination of POTs at this band generates a strongly oxidizing excited state which can accept a certain number of electrons from the organic substrate without decomposition. After oxidizing organic substrate, the photoreduced form of POT is usually reoxidized to its original oxidation state by an electron acceptor such as dioxygen. This reaction is the basis for the photocatalytic action of POTs [1,2].

One of the most promising POTs is the decatungstate anion  $\text{W}_{10}\text{O}_{32}^{4-}$ , which has been especially considered for its very important photocatalytic properties [5]. Considerable attention to this POT attributed to its  $\text{O} \rightarrow \text{W CT}$  absorption band at  $\text{W}–\text{O}–\text{W}$  bond which appeared at higher wavelength (324 nm) in comparison with other POTs [1,2]. Therefore, transition from the ground state to the excited state is easier for this POT. Otherwise, photoreduction of  $\text{W}_{10}\text{O}_{32}^{4-}$  in the presence of organic compounds produces directly reduced blue species  $\text{W}_{10}\text{O}_{32}^{5-}$ , which is reoxidized more rapidly by  $\text{O}_2$ . Another reason that makes the decatungstate very promising for synthetic purposes is that, in contrast to  $\text{TiO}_2$  semiconductor and other POTs, it does not induce any mineralization process of the substrate even after longer irradiation time. For these reasons, photoexcited decatungstate salts such as  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  and  $(n\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$  in the presence of  $\text{O}_2$  as a reoxidizing reagent have been extensively used as the homogeneous photocatalysts for oxidation of a variety of organic compounds, e.g. hydrocarbons, aliphatic alcohols, alkyl benzenes, amides, amines, aliphatic carboxylic acids and thioethers in homogeneous systems [6–17]. However, it is still difficult to separate these POTs from the reaction mixture because of their high solubility in polar media such as water and acetonitrile, which impedes their ready recovery and reuse.

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Therefore, considerable attention has been focused recently on heterogenization of POTs into inorganic solid networks such as silica and zeolites [18–22]. These systems make POTs easily handled and recycled.

In this paper, we report on the use of zirconia-supported sodium decatungstate,  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$ , as a novel and efficient heterogeneous photocatalyst for selective oxidation of a variety of alcohols into the corresponding carbonyl compounds under an  $\text{O}_2$  atmosphere at room temperature.

## 2. Experimental

All alcohols were either purchased commercially or synthesized as reported in the literature [23,24]. The light source was a 400 W high-pressure mercury lamp using a cutoff filter ( $\lambda \geq 320$  nm) while its temperature was maintained at  $25 \pm 2^\circ\text{C}$  by circulation of water through an external cooling coil.  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  was prepared according to the modified published procedure and characterized by UV–vis and IR spectroscopy as follows [8,25].  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  photocatalyst was also synthesized on the basis of the sol–gel method reported in literature for preparation of some of zirconia-supported POTs such as  $\text{Li}_5\text{PW}_{11}\text{TiO}_{40}/\text{ZrO}_2$  and  $\text{K}_7\text{PW}_{10}\text{Ti}_2\text{O}_{40}/\text{ZrO}_2$  with minor modification as follows [26].

### 2.1. Preparation of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ [8,25]

To a boiling solution containing  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (66 g) in distilled water (400 mL) was added 400 mL of a boiling aqueous 1 M HCl solution. The resulting solution was allowed to boil for 10 s, divided into two equal portions in 2-L beakers, and rapidly cooled to  $30^\circ\text{C}$  in a dry ice/methanol bath with stirring. Solid NaCl was added to near saturation, and the mixture was cooled further to  $0^\circ\text{C}$ . A precipitate formed which was collected and dried on a fritted funnel (33 g). This precipitate was suspended in hot acetonitrile (200 mL), the suspension was filtered, and the filtrate was placed in a freezer overnight. Large pale-lime crystalline rectangular blocks of  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  were collected and dried on a fritted funnel (11.2 g). The absorbance spectrum of  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  in acetonitrile consisted of well-defined maximum at 323 nm ( $\epsilon = 14100 \text{ M}^{-1} \text{ cm}^{-1}$ ) assigned to an  $\text{O} \rightarrow \text{W}$  LMCT transition [8,25]. The detected IR absorption bands of as synthesized  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  were  $958 \text{ cm}^{-1}$  (vibration of  $\text{W}=\text{O}$  bond),  $895$  and  $802 \text{ cm}^{-1}$  (vibration of  $\text{W}-\text{O}_b-\text{W}$  bond).

### 2.2. Preparation of $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$ [26]

The solution of zirconium (IV) *n*-butoxide (100 mmol, 38.32 g;  $\text{ZrO}_2$  content: 12.12 g) in EtOH (25 mL) was stirred at  $70^\circ\text{C}$ , and then the mixture was slowly cooled to ambient temperature. Afterward, the acidity of the mixture was adjusted to pH 2 by using hydrochloric acid. To the resulting mixture was dropwise added  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  (1.24 mmol, 3.08 g) dissolved in the mixed solution of 25 mL EtOH and 7.2 mL of water, which was maintained under constant stirring for 2 h until gelling. After gelation, the solids were filtered and dried in air at  $100^\circ\text{C}$  for 24 h. The dried gel was calcined in vacuum at  $200^\circ\text{C}$  for

4 h to fasten the zirconia network and washed with hot water ( $90^\circ\text{C}$ ) three times to give *ca.* 15 g of  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$ , as may have been expected. The IR and UV–vis spectra of this composite are similar with data reported for pure  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  in acetonitrile solution [8,25]. This indicates that the primary structure is retained after immobilizing the  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  into a zirconia matrix. The UV–vis diffuse reflectance spectrum (UV–vis/DRS) of  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  exhibited an absorption maximum at 325 nm assigned previously to the  $\text{O} \rightarrow \text{W}$  CT transition [8,25]. This band tailed into the visible region and disappeared around 420 nm. The photosensitivity and outstanding photocatalytic activity of this compound attributed to the existence of this broad band. The IR characteristic bands of  $\text{W}_{10}\text{O}_{32}^{4-}$  in the  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  composite appeared at  $945 \text{ cm}^{-1}$  (vibration of  $\text{W}=\text{O}$  bonds),  $885$  and  $798 \text{ cm}^{-1}$  (vibration of  $\text{W}-\text{O}_b-\text{W}$  bonds). The loading of  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  in the  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  composite was *ca.* 18.9 wt%, estimated by ICP-AES analysis.

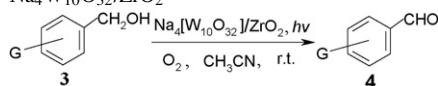
### 2.3. General procedure for photocatalytic oxidation of alcohols using $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$ under $\text{O}_2$

In a Pyrex flask equipped with a magnet bar, a solution of the alcohol (2 mmol) in acetonitrile (10 mL) was prepared. To this solution was added  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  (100 mg),  $\text{O}_2$  was allowed to flow and the flask was joined through an inlet tube to a balloon filled with  $\text{O}_2$  before irradiation. The reaction mixture was irradiated and oxidation of alcohols monitored by TLC and/or GC. After a suitable irradiation time, the irradiation was stopped and  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  was separated *via* filtration. The filtrate was concentrated and chromatographed on a silica-gel plate or column with *n*-hexane–EtOAc as the eluting solvent to give the carbonyl product. Yields are shown in Tables 1 and 2. The most products are commercially available and were identified through comparison of their physical and spectral data (m.p., TLC, IR,  $^1\text{H}$  NMR and/or  $^{13}\text{C}$  NMR and MS) with those of authentic samples. The products of entries 16–20 in Table 2 were characterized by comparing their m.p., IR,  $^1\text{H}$  NMR and MS data with literature data [27–31].

## 3. Results and discussion

First, the  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  composite, containing *ca.* 19 wt% of pure  $\text{Na}_4\text{W}_{10}\text{O}_{32}$ , was prepared through entrapment of  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  into a zirconia matrix via a sol–gel technique involving the hydrolysis of zirconium (IV) *n*-butoxide,  $\text{Zr}(\text{O}-n\text{-Bu})_4$ , as the  $\text{ZrO}_2$  source according to the reported procedure [8,25]. During the hydrolysis of  $\text{Zr}(\text{O}-n\text{-Bu})_4$  to hydrous zirconia gel at pH 2.0, the  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  molecules are entrapped in zirconia matrix. In this process,  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  composite is formed via electrostatic interactions and hydrogen bonding. In electrostatic interactions,  $\equiv\text{Zr}-\text{OH}$  groups in zirconia were protonated in an acidic medium to form  $\equiv\text{Zr}-\text{OH}_2^+$  groups, which should act as a counter ion for  $\text{W}_{10}\text{O}_{32}^{4-}$  polyanion, and yielded  $[\equiv\text{Zr}-\text{OH}_2^+]_x[\text{Na}_{4-x}\text{W}_{10}\text{O}_{32}^{x-}]$  by acid–base reactions. This interaction also existed in the silica-supported  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  composites, of which the preparation has been

Table 1  
Photocatalytic oxidation of substituted benzyl alcohols with O<sub>2</sub> catalyzed by Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/ZrO<sub>2</sub><sup>a</sup>

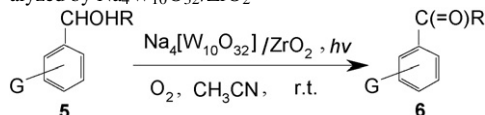


Entry	G	Irradiation time (h)	Yield of <b>4</b> (%) <sup>b</sup>
1	H	2	88
2	4-Me	1.25	95
3	2-Me	1.25	92
4	4- <i>iso</i> -Pr	1.25	95
5	4- <i>tert</i> -Bu	1.5	91
6	4-MeO	1	95
7	2-MeO	1.25	90
8	3-MeO	1.5	92
9	2,4-(MeO) <sub>2</sub>	1	96
10	3,4,5-(MeO) <sub>3</sub>	1	96
11	4-Ph	3	70
12	4-CF <sub>3</sub>	3.5	68
13	4-NO <sub>2</sub>	3.5	64
14	2-NO <sub>2</sub>	4	62
15	3-NO <sub>2</sub>	4.25	60
16	4-Cl	1.25	88
17	2-Cl	1.5	82
18	2,4-Cl <sub>2</sub>	1.2	92
19	4-Br	1.25	94
20	4-I	1.25	94

<sup>a</sup> Product identification was accomplished by comparison of their physical and spectral data (TLC, m.p., IR, <sup>1</sup>H NMR and or MS) with the known compounds.

<sup>b</sup> Isolated yield.

Table 2  
Photocatalytic oxidation of secondary benzylic alcohols and diols with O<sub>2</sub> catalyzed by Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/ZrO<sub>2</sub><sup>a</sup>



Entry	G	R	Irradiation time (h)	Yield of <b>6</b> (%) <sup>b</sup>
1	H	CH <sub>3</sub>	1	94
2	4-Me	CH <sub>3</sub>	1	97
3	4-NO <sub>2</sub>	CH <sub>3</sub>	3	76
4	H	C <sub>2</sub> H <sub>5</sub>	1	90
5	H	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	1.25	88
6	H	<i>cyclo</i> -C <sub>3</sub> H <sub>5</sub>	1.5	90
7	H	C <sub>6</sub> H <sub>5</sub>	1	94
8	4-Cl	C <sub>6</sub> H <sub>5</sub>	1.25	92
9	4-MeO	C <sub>6</sub> H <sub>5</sub>	1	95
10	4-MeO	4-MeOC <sub>6</sub> H <sub>4</sub>	1	95
11	4-NO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	3	72
12	4-Cl	4-ClC <sub>6</sub> H <sub>4</sub>	1.5	90
13	4-F	4-FC <sub>6</sub> H <sub>4</sub>	3	74
14	4-NMe <sub>2</sub>	4-NMe <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	1.25	94
15	H	C <sub>6</sub> H <sub>5</sub> C=O	2	75
16	H	CH <sub>2</sub> OH	1.5	76
17	4-Me	CH <sub>2</sub> OH	1	94
18	4-MeO	CH <sub>2</sub> OH	1	95
19	4-Cl	CH <sub>2</sub> OH	1.5	90
20	4-NO <sub>2</sub>	CH <sub>2</sub> OH	4	75

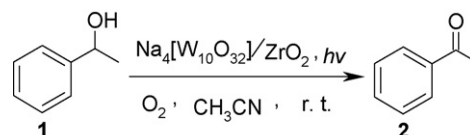
<sup>a</sup> All products were characterized on the basis of mass, IR and <sup>1</sup>H NMR spectral data and comparison with those of authentic samples or reported data.

<sup>b</sup> Isolated yield.

reported in literature [32]. We used them as the heterogeneous photocatalyst in our previous works [33]. The hydrogen bonding is formed in the composites between the oxygen atoms of the decatungstate and the surface hydroxyl groups of the zirconia network ( $\equiv\text{Zr}-\text{OH}$ ), which can be expressed in the forms of  $\text{W}=\text{O}_t \cdots \text{HO}-\text{Zr}\equiv$  and  $\text{W}-\text{O}_b \cdots \text{HO}-\text{Zr}\equiv$ , where  $\text{O}_t$  and  $\text{O}_b$  refers to the terminal oxygen atoms and the bridge oxygen atoms, respectively, in the decatungstate unit. These two interactions would ensure fixation of the  $\text{W}_{10}\text{O}_{32}^{4-}$  unit into the  $\text{ZrO}_2$  support firmly, so that the leaching of  $\text{W}_{10}\text{O}_{32}^{4-}$  in the liquid phase may be avoided. The IR characteristic bands of  $\text{W}_{10}\text{O}_{32}^{4-}$  in the  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  composite have some red shifts of *ca.* 10–13  $\text{cm}^{-1}$  compared with those for the parent  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  (see Section 2, e.g.  $\text{W}=\text{O}$  and  $\text{W}-\text{O}-\text{W}$  vibration bands). Therefore, it is confirmed that a strong chemical interaction, not simple physical absorption, exists between the polyanion and the zirconia surface. The  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  composite has a maximum UV–vis absorption peak at 325 nm similar to that of the parent  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  attributed to the oxygen-to-tungsten charge transfer absorption band for the  $\text{W}_{10}\text{O}_{32}^{4-}$  anions. This indicates that the primary structure of decatungstate is retained after immobilizing the  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  into a zirconia matrix.

The heterogeneous photocatalytic activity of the  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  composite was first tested via oxidation of 1-phenylethanol (**1**). We observed that when a heterogeneous mixture of this alcohol and a catalytic amount of  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  in acetonitrile was irradiated under an O<sub>2</sub> atmosphere with a high-pressure 400 W mercury lamp, acetophenone (**2**) was formed as the only photoproduct in 94% yield within 1 h (Scheme 1).

Using unsupported  $\text{Na}_4\text{W}_{10}\text{O}_{32}$ , we found that 68% of **1** was oxidized to **2** within 1 h under the same conditions. When the pure  $\text{ZrO}_2$  support was used as a heterogeneous photocatalyst for aerobic oxidation of **1**, less than 10% of **2** was formed after 2 h irradiation, suggesting that the photocatalytic activity of the  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  system is mainly due to  $\text{Na}_4\text{W}_{10}\text{O}_{32}$ . These findings confirm that the photoactivity of  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  composite is higher than that of the starting  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  cluster and zirconia support. This is due to (i) higher specific surface area of composite than that of the starting cluster and zirconia support and (ii) the synergistic effect of the  $\text{W}_{10}\text{O}_{32}^{4-}$  unit and the  $\text{ZrO}_2$  support. That is, recombination of photogenerated hole ( $\text{h}^+$ ) and electron ( $\text{e}^-$ ) in the  $\text{ZrO}_2$  semiconductor is inhibited by the photoexcited  $\text{W}_{10}\text{O}_{32}^{4-}$  unit, therefore, the photoactivity of the composite was improved [26]. No oxidation products were observed when blank experiments were run in the dark and or in the absence of  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$ . On the other hand, when suspension of  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  in acetonitrile in the presence of **1** was irradiated under inert atmosphere



Scheme 1. Photocatalytic oxidation of 1-phenylethanol to acetophenone over  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$ .

(N<sub>2</sub>), it rapidly became blue, indicating the formation of reduced decatungstate, W<sub>10</sub>O<sub>32</sub><sup>5-</sup> [7,9]. Under this condition, GC analysis indicated that a trace amount of **2** (<5%) was obtained and about 95% of the starting **1** was recovered even after a long irradiation time (4 h). This observation confirms that O<sub>2</sub> plays an important role in the reoxidation of the reduced form of decatungstate and therefore, in completion of the photocatalytic cycle.

Recovery of the Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/ZrO<sub>2</sub> is easy; that is, this photocatalyst is separated by simple filtration after the reaction. At the same time, the concentration of W in the filtrate was found less than 1% by ICP-AES. Indeed, the recovered photocatalyst was used for recycling and deactivation of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/ZrO<sub>2</sub> was hardly observed in the oxidation of **1** even after seven catalytic cycles. On the other hand, when the catalyst was separated from the reaction mixture shortly (0.5 h) after the beginning of irradiation and the reaction filtrate was further irradiated under O<sub>2</sub>, no extra formation of **2** was observed *via* GC analysis even after 4 h. All these findings confirm that the present photoreaction catalyzed by Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/ZrO<sub>2</sub> is heterogeneous in nature. Therefore, although during this study we found that the pure Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> in homogeneous system also catalyzes the oxidation of benzylic alcohol such as **1** in moderate yield under O<sub>2</sub>, our results focused on oxidation these substrates in the presence of the Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/ZrO<sub>2</sub> system that permits recycling and reuse of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>. Also, leaching of W<sub>10</sub>O<sub>32</sub><sup>4-</sup> cluster from the zirconia support into the reaction system was hardly observed during the photocatalytic reactions, attributed to the strong chemical interactions between the W<sub>10</sub>O<sub>32</sub><sup>4-</sup> units and the zirconia support. Under similar conditions to **1**, the photolysis of a series of primary and secondary benzylic alcohols in the presence of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/ZrO<sub>2</sub> was studied. We found that these substrates were efficiently oxidized to the corresponding carbonyl compounds in high yields without over-oxidation of the benzaldehydes to carboxylic acids. The results are presented in Tables 1 and 2.

As can be seen in Table 1, the oxidation a variety of ring-substituted benzyl alcohols having various substituents, e.g. Me-, *iso*-Pr-, *tert*-Bu-, -OMe, -NO<sub>2</sub>, -CF<sub>3</sub> and halogens with O<sub>2</sub> was investigated over Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/ZrO<sub>2</sub>. These alcohols were selectively converted to their corresponding aldehydes in moderate to high yields without overoxidation to carboxylic acids (Table 1, entries 2–20). In comparison with benzyl alcohol (Table 1, entry 1), electron-donating groups accelerate the reaction (Table 1, entries 2–10) whereas electron-withdrawing groups slow down it (Table 1, entries 11–15). Halogenated benzyl alcohols gave the corresponding aldehydes in high yields (Table 1, entries 16–20).

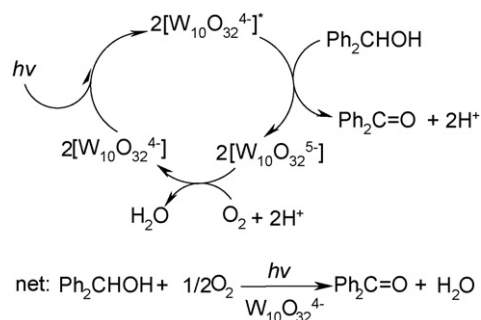
Under our reaction conditions, various secondary benzylic alcohols were also converted with high selectivity to their corresponding ketones (Table 2, entries 1–15). The electronic effect observed for primary benzylic systems also seemed to be prevalent in the case of secondary benzylic systems. 1-(*p*-Nitrophenyl)ethanol (Table 2, entry 3) required a longer reaction time and gave a decreased yield when compared to more electron-rich secondary benzylic substrates, e.g. 1-(*p*-methylphenyl)ethanol (Table 2, entry 2).

Furthermore, heteroaromatic alcohols such as pyridine-4-methanol and thiophene-2-methanol were converted to the corresponding aldehydes in 76 and 80% yields, respectively, without oxidation of N and S heteroatoms during 4 h irradiation. This reaction is also efficient for allylic systems. For example, cinnamyl alcohol gave cinnamaldehyde in 82% yield after 2 h irradiation whereas the carbon–carbon double bond remained intact.

In contrast, aliphatic and aryl-substituted non-benzylic alcohols such as 2-propanol, 1-heptanol, 1-octanol, 2-octanol and 3-phenyl-1-propanol are oxidized into the corresponding carbonyl compounds with much lower efficiency under the same reaction conditions. The GC yields of these conversions were in the range of 14–26% albeit after very long irradiation times (12 h). This observation suggested a possible chemoselective oxidation of benzylic alcohols in the presence of non-benzylic alcohols. Therefore, when a 1:1 mixture of 1-phenylethanol and 2-phenylethanol was irradiated in the presence of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/ZrO<sub>2</sub> under O<sub>2</sub>, the former was oxidized to acetophenone in 93% GC yield and the latter gave 2-phenylacetaldehyde in <5% GC yield after 1 h. The competitive oxidation of benzyl alcohol and 2-phenylethanol exhibits a similar degree of selectivity. We next turned to the synthetically more useful case of intramolecular competition between benzylic and non-benzylic alcoholic hydroxy groups in *vic*-diols (Table 2, entries 16–20). It was observed that these diols were cleanly oxidized to  $\alpha$ -ketols without cleavage of the 1,2-diol bond in high yields. However, the non-benzylic OH groups were also oxidized to carbonyl groups under long irradiation times (>5 h) albeit with much low efficiency.

The experiments, usually performed on a 2 mmol scale, can be scaled up to 100 mmol of alcoholic substrate without difficulties in the presence of photocatalyst (100 mg). For example, 50 mmol of 4-methoxybenzyl alcohol provided the corresponding aldehyde in 95% isolated yield within 2.5 h irradiation and 100 mmol of 1-phenylethanol gave acetophenone in 92% isolated yield after 3.25 h using the present procedure.

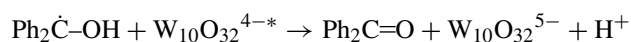
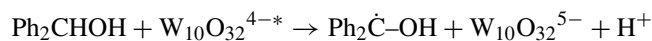
From the above facts and the results presented in Table 1, together with literature data [6–17], the course of events following light absorption by W<sub>10</sub>O<sub>32</sub><sup>4-</sup> in Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/ZrO<sub>2</sub> composite can be explained *via* the following photocatalytic cycle using benzhydrol (Ph<sub>2</sub>CHOH) as a prototype substrate (Scheme 2).



Scheme 2. The photocatalytic cycle for oxidation of benzhydrol by W<sub>10</sub>O<sub>32</sub><sup>4-</sup> in Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub>/ZrO<sub>2</sub> composite.



As indicated in the above mechanism, it seems that the formation of the one-electron reduced form of decatungstate,  $W_{10}O_{32}^{5-}$ , in the presence of an alcoholic substrate involves hydrogen-atom abstraction from the alcohol by photoexcited decatungstate,  $W_{10}O_{32}^{4-*}$ , followed by rapid electron transfer according to the following reactions



On this basis, photooxidation of alcohols is mainly due to hydrogen transfer rather than electron transfer. The following facts confirm this mechanism: (a) when the tertiary benzylic alcohols such as triphenylmethanol and 2-phenyl-2-propanol which possess no H-atom at the benzylic position were examined as the substrate under our reaction conditions, the starting materials were recovered quantitatively even after 6 h irradiation. (b) Also, the observation described above that 1-phenylethanol reacts very much faster than 2-phenylethanol is also consistent with a hydrogen-atom abstraction mechanism. (c) Indeed, work done by Ward et al. [34] supports this mechanism, which shows a deuterium isotope effect in the acetone production,  $k_H/k_D=3.7$  when deuterated  $Me_2CDOH$  is photolyzed with  $Mo_7O_{24}^{6-}$ .

According to the mechanism, species showing the high reactivity for oxidation have easily removable or abstractable H-atoms. Therefore, primary and secondary alcohols with benzylically activated C–H bonds in the present work act as good photoreducing reagents and oxidized in an efficient way. The observed selectivity for the oxidation of *vic*-diols at benzylic position can be also attributed to the ease of dissociation of benzylic active C–H bond in comparison with non-benzylic C–H bonds. Such a simple mechanistic proposal accommodated the observation that highly activated, benzylic alcohols were good substrates due to the enhanced lability their  $\alpha$ -hydrogen atoms. In contrast, aliphatic alcohols are far less reactive toward H-radical abstraction, and accordingly, very poor conversions should ensue.

#### 4. Conclusion

In conclusion, a novel, efficient and environmentally benign photocatalytic method is presented for the oxidation of activated alcohols to aldehydes and ketones by  $O_2$  in the presence of  $Na_4W_{10}O_{32}/ZrO_2$  composite as a recyclable heterogeneous photocatalyst which is important for synthetic organic chemists. No other over-oxidized compounds were detected. Benzylic hydroxy group can be efficiently converted into corresponding carbonyl in the presence of non-benzylic hydroxy groups. It is noteworthy that catalyst can be used for subsequent cycles of oxidation without any release of the polytungstate during the experiments, and without any loss of its photocatalytic activity. It seems most likely that the primary reaction between  $W_{10}O_{32}^{4-*}$  and alcoholic substrates involves hydrogen-atom abstraction prior to electron transfer. The present work provided a new type of heterogeneous photocatalytic materials for potential applications in synthetic organic chem-

istry. Study on detailed mechanism and also photocatalytic applications of  $Na_4W_{10}O_{32}/ZrO_2$  and similar composites to oxidation of other organic substrates are now in progress in our laboratory.

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