

Sol-Gel Silica-Supported 12-Tungstosilicic Acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$) as a Heterogeneous Photocatalyst for Efficient and Selective Oxidation of Benzylic Alcohols with O_2 under Photoirradiation

Saeid Farhadi,* Zaynab Babazadeh and Mansoureh Maleki

Department of Chemistry, University of Lorestan, Khoramabad, Iran

E-mail: farhadi.s@lu.ac.ir

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Abstract

Sol-gel silica-supported heteropolyoxotungstate ($\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$), prepared by incorporating $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ cluster into a silica matrix *via* sol-gel technique, was used as an efficient heterogeneous photocatalyst for oxidation of alcohols by O_2 . Irradiation of a series of primary and secondary benzylic alcohols in acetonitrile solvent over $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ under O_2 atmosphere resulted in the corresponding aldehydes and ketones selectively and in high yield. 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. Eventually, heterogeneous photocatalyst considerably is more active than the unsupported $\text{H}_4\text{SiW}_{12}\text{O}_{40}$.

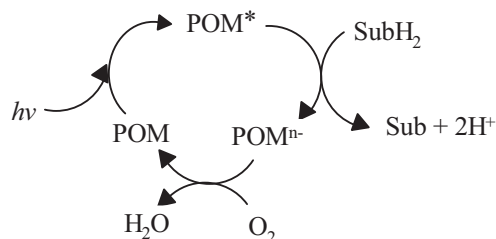
Key words: Photooxidation, Benzylic alcohols, Heterogeneous, Polyoxometalates, Photocatalyst, Sol-gel silica-supported.

Introduction

The importance of environmentally friendly processes has been recognized over all fields of industry and, needless to say, in the field of synthetic organic chemistry as well. In this context, photochemical processes that take place under mild conditions, i.e. room temperature and atmospheric pressure or, even more, photocatalytic ones that avoid stoichiometric reagents and consume cheap photons are particularly attractive for synthetic purposes from an economic and environmental point of view.¹ In recent years, the semiconductor metal oxides (mainly TiO_2) widely used as green photocatalyst in the field of synthetic organic chemistry.^{2–4} However, the TiO_2 photocatalysis method generally leads to the total mineralization of organic compounds into CO_2 and H_2O . Moreover, the ultrafine TiO_2 particles used are easy to lose and it is difficult to separate them from the reaction systems due to the formation of a milky dispersion of the TiO_2 particles. These findings suggest that the development of other photocatalytic materials is important.

Another class of photochemically active materials that has received less attention, in comparison with semiconductors, are the polyoxometalates (POMs).⁵ Many of them, such as $\text{W}_{10}\text{O}_{32}^{4-}$, $\text{Mo}_7\text{O}_{24}^{6-}$, $\text{PW}_{12}\text{O}_{40}^{3-}$, $\text{PMo}_{12}\text{O}_{40}^{3-}$ and $\text{SiW}_{12}\text{O}_{40}^{4-}$, share the same general photochemical characteristics of the semiconductor

photocatalysts, that is, they can be photoexcited (POM^*), abstract one or two electron(s) from organic substrate without decomposition (POM^n), be reoxidized and return to their original oxidation state (POM) by electron acceptors, such as the dissolved dioxygen in solution. Thus, they complete a net photocatalytic cycle. The proposed photocatalytic cycle of POMs, which is analogous to the well-known photocatalytic cycle of semiconductor photocatalysts, is shown in Scheme 1.^{6–9}



Scheme 1. The photocatalytic cycle of a polyoxometalate (POM). POM^* = Photoexcited POM, POM^n = Reduced POM, SubH_2 = Organic substrate, Sub = Oxidized substrate.

The photocatalytic oxidation of organic substrates by POMs has been studied extensively in homogeneous systems and it indicates that the photo-oxidation efficiency of POMs is comparable to that of the semiconductor TiO_2 .^{10–17} The major drawback to the practical applications of POM photocatalytic systems

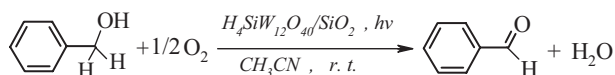
is the high solubility of them in water and in highly polar organic media which impedes ready recovery and reuse of the photocatalyst.^{18,19} Moreover, the specific surface area of the solid POMs is very low ($<10 \text{ m}^2/\text{g}$), leading to very few active sites on their surfaces.²⁰ Thus, immobilization of POMs onto solid support to create heterogeneous photocatalysts is necessary for their recovery and possibly their recycling. Moreover, their catalytic activities may be improved. In this framework, the POMs $\text{Na}_4\text{W}_{10}\text{O}_{32}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ supported into porous inorganic solids e.g. silica or zeolite networks have been used as the effective and recyclable photocatalysts for photo-degradation and mineralization of aqueous organic pollutants.^{21–30} However, there are less report regarding the application of supported POMs as the photocatalysts for synthetic organic chemistry, so far.^{31–32}

In the present work, the sol-gel silica-supported $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ was used, for the first time, as an efficient and recyclable heterogeneous photocatalyst for aerobic oxidation of various primary and secondary benzylic alcohols into the corresponding carbonyl compounds. In addition, the photocatalytic behaviour of the $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ composite was also compared with pure $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ in homogeneous system.

Results and discussion

The silica-supported polyoxometalate, $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$, containing *ca.* 20 wt. % of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ was synthesized through encapsulating into a silica matrix on the basis of the sol-gel method reported recently, by adding $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ during the hydrolysis of tetraethyl orthosilicate ($\text{Si}(\text{OEt})_4$, TEOS) as the SiO_2 source.^{18,21} During TEOS hydrolysis-condensation sol-gel process in the presence of this POM, the $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ molecules were entrapped in silica matrix. Photocatalytic activity of the supported $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ was tested *via* oxidation of a series of various benzylic alcohols under O_2 atmosphere.

The oxidation of benzyl alcohol was first investigated as a standard substrate using $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ under O_2 atmosphere in acetonitrile. It was found that the benzyl alcohol was oxidized to benzaldehyde in 82 % yield within 4 h irradiation and *ca.* 16 % of the benzyl alcohol was recovered (Scheme 2).



Scheme 2. Aerobic oxidation of benzyl alcohol.

On the other hand, when the pure SiO_2 support was used as a catalyst for aerobic oxidation of benzyl

alcohol, no observable oxidation product was detected from GC analysis after 4 h irradiation, suggesting that the photocatalytic activity of the $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ system is due to $\text{H}_4\text{SiW}_{12}\text{O}_{40}$. Control experiments without $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ or light under same reaction conditions showed no reaction. Using pure $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, as a homogeneous photocatalyst, we found from GC analysis that 35 % of the benzyl alcohol was oxidized to benzaldehyde and about 64 % of benzyl alcohol was recovered within 4 h irradiation under the same reaction conditions. These results clearly indicate that silica-supported $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ is much more reactive than the bulk $\text{H}_4\text{SiW}_{12}\text{O}_{40}$. The significantly higher activity of $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ composite, as compared with that of unsupported $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, is attributed to the much higher density of active sites in $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$.

Only a small amount of benzaldehyde from photooxidation of benzyl alcohol was observed when the reaction with $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ was carried out under N_2 and almost concomitantly, $\text{SiW}_{12}\text{O}_{40}^{5-}$ was obtained, as evidenced from the appearance of a dark blue colour in the reaction suspension. The blue colour was also observed when benzhydrol was used as the substrate. Since there is no catalyst regeneration, according with Scheme 1 in the absence of O_2 , the photoexcited $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ stoichiometrically oxidizes the alcohol to aldehyde with the negligible yield. Therefore, it is confirmed that $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$, light and O_2 are essential for this reaction. A decrease in catalytic activity and selectivity for benzaldehyde was not observed, providing 79 % yield of benzaldehyde even after being reused five times.

The fact that the reaction solution contained no dissolved $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, which was determined by UV-VIS, IR and ICP-AES, confirms that this POM did not leach from the silica support during the photocatalytic reaction. No leaching of entrapped catalyst is important since many heterogeneous oxidations can actually be promoted by catalyst leached in solution.³³ Further evidence that confirms that the reaction mediated by the catalytic amount of $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ is heterogeneous in nature drawn from the fact that when the catalyst separated from the reaction mixture shortly (30 min) after the beginning of the irradiation and the reaction filtrate was irradiated under O_2 , no extra formation of benzaldehyde from benzyl alcohol was observed *via* GC and/or TLC even after 4 h irradiation.

Under the explored standard conditions, a range of primary and secondary alcohols such as aliphatic, benzylic, allylic and even sulfur/nitrogen containing alcohols were evaluated as substrates for the aerobic oxidation. All the tested primary benzylic alcohols were converted into their corresponding aldehydes and no overoxidation to acids was observed in the case of aldehyde products. (Table 1).

Table 1. Photooxidation of various benzylic alcohols with O₂ catalysed by H₄SiW₁₂O₄₀/SiO₂

$$\text{Ar}-\text{CH}_2\text{OH} \xrightarrow[\text{O}_2, \text{CH}_3\text{CN}, r. t.]{\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2, h\nu} \text{Ar}-\text{CHO}$$

Entry	Alcohol	Product ^a	Time (h)	Yield (%) ^b
1			4	82
2 ^c			4	35
3			2	95
4			2	88
5			2	88
6			2.5	80
7			1.5	95
8			1.25	92
9			2	86
10			1.5	90
11			2	88
12			6	35
13			6	30
14			4	74
15			4	78
16			4	76
17			3	80
18			4	66
19			4	74
20			4	70
21			3	80
22			6	30
23			6	32
24			12	56

^a All products were characterized on the basis of mass, IR and ¹H-NMR spectral data. ^b Yields are for isolated and chromatographically pure products. ^c Unsupported H₄SiW₁₂O₄₀ was used as the photocatalyst.

Benzylic alcohols having electron-donating groups such as Me-, MeO-, tert-Bu-, iso-Pr in the aromatic ring and also halobenzyl alcohols were oxidized to corresponding aldehydes in excellent yields (Table 1, entries 3-11). However, 4-nitro- and 4-trifluoromethylbenzyl alcohols which possess an electron-withdrawing group, resisted this oxidation conditions, and the corresponding benzaldehydes were formed in 35 and 30 % yields respectively after 6 h irradiation (Table 1, entries 12 and 13). Furthermore, furfuranol, thiophene-2-methanol and pyridin-4-methanol, were oxidized to the corresponding aldehydes in high yields and heteroatoms such as S or N did not result in any

Table 2. Photooxidation of secondary benzylic alcohols and vicinaldiols with O₂ catalysed by H₄SiW₁₂O₄₀/SiO₂

Entry	Alcohol	Product ^a	Time(h)	Yield (%) ^b
1			1.5	92
2 ^c			1.5	30
3			1	98
4			1.25	95
5			1.5	90
6			1.5	86
7			1	94
8			1.5	85
9			2.5	78
10			1.5	86
11			1.5	85
12			1.25	90
13			2	60
14			2.5	75

^a All products were characterized on the basis of mass, IR, and ¹H-NMR spectral data. ^b Yields are for isolated and chromatographically pure products. ^c Unsupported H₄SiW₁₂O₄₀ was used as the photocatalyst.

notorious effects on the catalytic system (Table 1, entries 14-16). Other Arylmethyl alcohols gave the corresponding benzaldehydes in good yields (Table 1, entries 17-20). Allylic alcohol such as cinnamyl alcohol was also good substrate, and in this case no isomerisation of the conjugated double bond was observed (entry 21)

Whereas various primary benzylic and allylic alcohols were oxidized in a highly efficient way, non-benzylic arylalcohols such as 2-phenylethanol and 3-phenyl-1-propanol were less reactive and the corresponding aldehydes were obtained in 30-32 % yields (Table 1, entries 22 and 23) and therefore longer irradiation time was required to obtain the aliphatic carbonyl compound in moderate yield (entry 24).

With this method, various secondary benzylic alcohols were converted with high selectivity to their corresponding ketones and were more efficient than the primary benzylic alcohols (Table 2, entries 1-9). This reaction is highly selective for vicinaldiols in oxidizing only the secondary hydroxy group α to the benzene ring (Table 2, entries 10-14). Therefore, it is a method of choice for the oxidation of benzylic OH in the presence of non-benzylic OH.

To study the possible chemoselectivity, a mixture of 1-phenylethanol and 2-phenylethanol was next

subjected to 1 h photoirradiation in the presence of $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ under O_2 , GC analysis indicated that the former was oxidized to acetophenone in 84 % yield and the latter gave 2-phenylacetaldehyde in < 5 % yield. This study clearly reveals that this method can be applied for the efficient oxidation of benzylic alcohols in the presence of non-benzylic alcohols. However, upon prolonged irradiation (6 h) of this mixture, 2-phenylethanol formed aldehyde in 25 % yield.

Conclusions

In conclusion, a novel, efficient and environmentally benign photocatalytic method is presented for the oxidation of alcohols to aldehydes and ketones. This methodology is also compatible in the presence of other functionalities such as methoxy, nitro, halogen and alkene double bonds. Benzylic alcohols can be chemoselectively converted into corresponding carbonyl compounds in the presence of non-benzylic hydroxy groups. Heterocyclic alcohols are also selectively oxidized without oxidation of heteroatoms like N, S. It is noteworthy that the aldehydes do not undergo further oxidation to carboxylic acids. In addition, it is easy to separate and recover the catalyst for another photocatalytic recycling. The present work provided a new type of heterogeneous photocatalytic materials for potential synthetic application.

Experimental

Preparation of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ was adapted from the literature methods.³⁴ Alcohols were either purchased commercially or synthesized as reported in the literature.^{35, 36} The light source was a 400W high-pressure mercury lamp (HPML, $\lambda > 320$ nm).

Preparation of the $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$:

The $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ photocatalyst was prepared by the improved literature methods.^{18,21} To a mixture of water (2 mol), 1-BuOH (0.2 mol) and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (1.04×10^{-3} mol, 3g), was added tetraethyl orthosilicate (TEOS, 0.2 mol), and the mixture was stirred at 80 °C for 3 h. The hydrogel thus obtained was dehydrated slowly at 80 °C for 3 h and dried in a vacuum at 60 °C for 12 h. The dried gel was calcined in a vacuum at 150 °C for 2 h to fasten the silica network and gave ca. 15 g of silica-included heteropolyacid, as may have been expected. The spectra of IR, UV-VIS and ICP-AES analysis are in agreement with data reported for this composite.^{18,21} The loading of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ in the $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ composite was ca. 20 %, estimated by ICP-AES analysis. The silica-included $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ was dried in a vacuum at 150 °C for 3 h prior to use for photocatalytic reactions.

General procedure for photocatalytic oxidation of benzylic alcohols by using $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ under O_2 :

A solution of benzylic alcohol (1 mmol) in acetonitrile (25 mL) was added to a Pyrex cell containing a teflon-coated stirring bar. To this solution was added $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ (100 mg). Oxygen was passed through, and the reaction mixture was kept under an oxygen atmosphere (O_2 balloon). The suspension was vigorously stirred and irradiated. The temperature of the suspension was maintained at 25 ± 2 °C by water circulation through an external cooling coil. The reaction was followed by TLC and/or GC and after an appropriate irradiation time, the photocatalyst was filtered off. After removal the solvent, the products were purified by silica-gel plate or column chromatography. Yields are shown in Table 1. All of the products were characterized by mass, IR and ^1H -NMR spectra and by comparison with the known compounds.³⁷⁻⁴¹

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Povzetek

S sol-gel tehniko smo pripravili 12-volframsilicijevo kislino na podlagi silicijevega dioksida ($H_4SiW_{12}O_{40}/SiO_2$) in produkt uporabili kot učinkovit heterogen fotokatalizator za oksidacijo alkoholov z O_2 . Pri obsevanju vrste primarnih in sekundarnih benzilnih alkoholov v acetonitrilu kot topilu v prisotnosti $H_4SiW_{12}O_{40}/SiO_2$ v kisikovi atmosferi smo dobili ustrezne aldehide in ketone z visokim izkoristkom. Alkoholi brez benzilne skupine so manj reaktivni pod opisanimi pogoji. Fotokatalizator smo uporabili večkrat brez znatnega zmanjšanja aktivnosti in selektivnosti. Heterogeni katalizator ima znatno višjo aktivnost kot $H_4SiW_{12}O_{40}$ brez sol-gel podlage.