

# Photocatalytic selective aerobic oxidation of alcohols to aldehydes and ketones by HPW/MCM-41 in ionic liquids

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## Abstract

The selective oxidation of alcohols with molecular oxygen was efficiently completed in high conversion and selectivity using HPW/MCM-41 as a heterogeneous photocatalyst in ionic liquids, [bmim]PF<sub>6</sub>, [omim]BF<sub>4</sub> and [hmim]BF<sub>4</sub>. Comparative studies on the catalytic properties of HPW/MCM-41, HPW to MCM-41 were carried out. Some important variables, e.g. the loading amount of HPW on MCM-41 and the effects of different ionic liquids were discussed in this work.

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## 1. Introduction

The oxidation of alcohols into corresponding aldehydes and ketones is a crucial transformation in organic chemistry, with both academic and industry relevance [1–4]. Traditionally, this reaction is realized by using inorganic oxidants (e.g. Cr(VI) reagents). These reagents, which are neither environmental friendly nor economical, are needed in stoichiometric amounts and hard to be separated from products. Moreover, most of the traditional catalysts are not effective for a broad range of alcohols, especially those in the presence of other oxidizable functional groups such as olefinic group and heteroatoms [5]. To obtain suitable green aerobic oxidation catalysts is a significant challenge. Recently, more and more efforts have been put into highly valuable catalytic oxidizing processes. Protocols based on O<sub>2</sub>, air or H<sub>2</sub>O<sub>2</sub> [6–9] are particularly attractive because of cheap and readily available oxidants. Successful examples include both homogeneous catalysts (e.g. Ru-, Pd-,

Cu-complexes; bi-metallic complexes systems) and heterogeneous catalysts (e.g. metal catalysts and supported catalysts, including mesoporous materials, zeolites, polymer-supported catalysts, etc.) [10]. Among these, the development of photocatalysts is receiving much attention recently. TiO<sub>2</sub> [11] and photo-Fenton reagents [12] are most well-known examples, which are able to catalyze the oxidation of various organic compounds. However, searching for suitable green aerobic photooxidation catalysts is still a great challenge, especially for selective oxidation of alcohols.

Polyoxometalates (POMs) is an important class of photocatalysts, which has received attention in recent years [13]. Owing to their photo-properties at near UV–vis area, under UV–vis irradiation, polyoxometalates generate an O to M (M = W and Mo) charge-transfer excited state, which has strong oxidation ability for the oxidation of organic substrates. As a result, photoexcited POMs are reduced by the transfer of one or two electron(s) from the organic substrate. The 12-tungstophosphoric acid H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (HPW) was found to be the most acidic of the Keggin series [14]. Most reports on its catalytic properties were based on its acidic property. It was found that when this acid was supported on a carrier with large surface area, its catalytic performance was improved [15,16]. We previously reported a series of HPW/MCM-41 systems for the alkylation reaction

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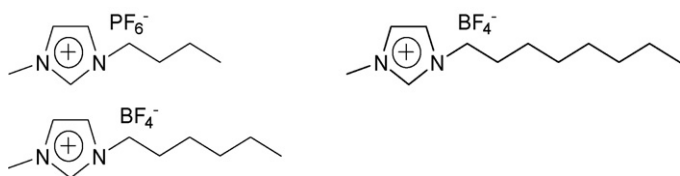


Fig. 1. Structure of ionic liquids 1–3: (a) [bmim]PF<sub>6</sub>, (b) [omim]BF<sub>4</sub> and (c) [hmim]BF<sub>4</sub>.

of phenol with TBA [17]. Recently, Farhadi et al. reported an HPW/SiO<sub>2</sub> system for the photocatalytic oxidation of alcohols [18]. However, to our knowledge, HPW/MCM-41 systems as photocatalysts of the selective oxidation of alcohols have not yet been reported.

Room-temperature ionic liquids [19] are finding growing applications as alternative reaction media for separations [20] and organic transformations [21–28]. Recent examples of such organic transformations include hydrogenations [21], Friedel–Crafts reactions [22], Diels–Alder reactions [23], Heck reactions [24], Bischler–Napieralsky reactions [25], olefin dimerizations [26], cross-couplings [27], hydroformylations [28] and alkylations [16d, 17]. The desirable advantages of ionic liquids such as low vapor pressure, wide liquid range and thermal stability have made them exceptional reaction media. Accordingly, they are emerging as novel replacements for volatile organic compounds, mainly used as solvents in organic transformations. Ionic liquids have already been used as solvents for oxidation of alcohols with hypervalent iodine reagents, the Cu(ClO<sub>4</sub>)<sub>2</sub>/acetamido-TEMPO/DMAP catalytic system, tetravalent cerium salts as oxidizing agents, manganese dioxide, etc. [29]. The main purpose of current work is to investigate the photocatalytic oxidation properties of HPW/MCM-41 and the effects of ionic liquids for the photocatalytic oxidation procedure.

In this paper we report the selective oxidation of alcohols by a series of HPW/MCM-41 as photocatalysts with an enhanced activity in the presence of ionic liquids, such as [bmim]PF<sub>6</sub> (**IL1**), [omim]BF<sub>4</sub> (**IL2**) and [hmim]BF<sub>4</sub> (**IL3**) (Fig. 1). For comparison, the occurrence of the reaction was also investigated in traditional organic solvents catalyzed by HPW and MCM-41. The loading amount of HPW on MCM-41 and the effects of different ionic liquids were intensively discussed in this work.

## 2. Experimental

### 2.1. Materials

Ionic liquids **1**, **2**, **3** (**IL1**, **IL2**, **IL3**) were purchased from Solvent-Innovation GmbH and purified by washing with ethyl acetate and diethyl ether, and dried in vacuum. All the alcohols, with purity higher than 99%, were purchased from Fluka and used as received.

The preparation of three HPW (*x*%) /MCM-41 catalysts (where *x*% is the respective HPW content of 15, 30 and 50 wt%) were reported elsewhere [16c].

### 2.2. Catalytic reaction

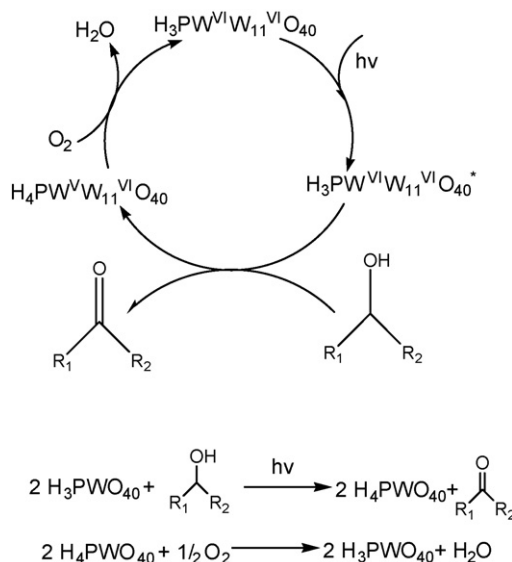
The experimental procedures for the studied eight substrates with a wide range of primary, secondary, allylic and benzylic alcohols were similar. The oxidation of cinnamyl alcohol carried out in **IL2** with HPW (30%)/MCM-41 as catalyst was taken as an example.

To a 25 mL two-necked flask, 1 mL ionic liquid and HPW (30%)/MCM-41 catalyst (0.01 g) were added. Cinnamyl alcohol (0.0134 g, 1 mmol) was added successively. The mixture was vigorously stirred at room temperature, while O<sub>2</sub> was gently bubbled through the reaction mixture. The reaction was irradiated with a high pressure 400 W mercury lamp. In order to monitor the reaction, samples were taken at intervals, treated with passing through a silica gel pad and diluted with toluene before injecting in GC. Qualitative analyses were conducted with an HP 6890N/5973N GC–MS with chemstation containing a NIST Mass Spectral Database. Quantitative analyses were conducted with an HP 6890 GC equipped with an FID. The conversion was measured by gas chromatography. An HP-5 capillary column containing crossed linked 5% phenyl–95% dimethylsiloxane copolymer was used for GC separation.

After the reactions have been finished after certain reaction time, determined by GC monitoring, the post-reaction system was cooled down to room temperature and filtered. The filtrate was washed with toluene. The organic phase was then dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The residual crude reaction mixture was purified by silica-gel column chromatography to give the pure products.

## 3. Results and discussion

The photocatalytic property of HPW is due to its Keggin structure. The metal ions (W<sup>VI</sup>) in HPW have d<sup>0</sup> electronic configurations. Upon irradiation by UV, electrons are promoted from the low energy electronic states to the high-



Scheme 1. Presumed photocatalytic process of HPW on alcohols.

energy electronic states. The only absorption band, which occurs in the UV–vis range of the electronic spectrum, is due to the oxygen-to-metal ( $O \rightarrow M$ ) ligand-to-metal charge transfer (LMCT). Irradiation of HPW ( $H_3PW^{VI}W_{11}^{VI}O_{40}$ ) generates electron–hole pairs, producing a transitional form  $HPW^*$  ( $H_3PW^{VI}W_{11}^{VI}O_{40}^*$ ). As the hole migrates to the particle surface, it interacts with the primary and secondary alcohols, producing the reductive state of HPW ( $H_4PW^VW_{11}^{VI}O_{40}$ ).  $H_4PW^VW_{11}^{VI}O_{40}$  further reacts with dissolved  $O_2$ , ultimately making water and itself returns to the oxidative state ( $H_3PW_{12}^{VI}O_{40}$ ). The reaction process can be described in

**Scheme 1.** In this reaction, primary and secondary alcohols are electronic donors, the photoredox reactions of HPW proceeding effectively in the presence of primary and secondary alcohols. HPW is firstly irradiated by UV, and reaches to an excited state. One molecule of alcohol photochemically reduces two molecules of HPW and itself is oxidized to aldehyde or ketone. In the presence of oxygen, the thermal oxidation of the reduced HPW species takes place at room temperature.

Based on the property of this photocatalytic reaction, many variables, which may affect the reaction, need to be considered, such as, the amount of HPW, irradiation energy and time, sub-

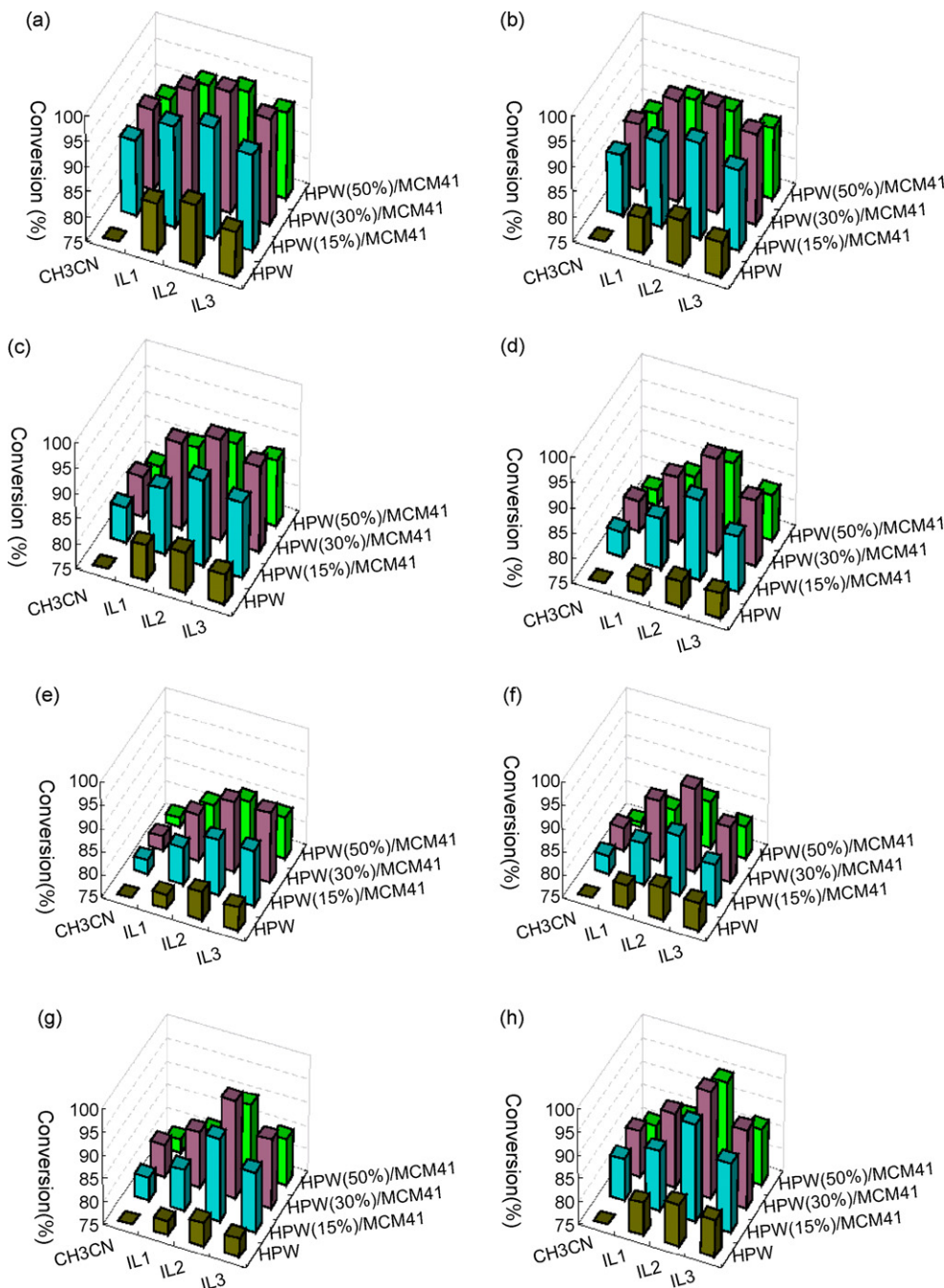
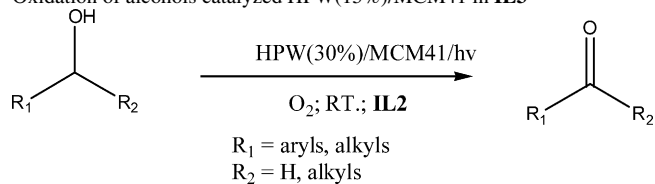


Fig. 2. Conversion of the alcohols (substrates 1–8) under different catalytic conditions. (a) Substrate 1, (b) substrate 2, (c) substrate 3, (d) substrate 4, (e) substrate 5, (f) substrate 6, (g) substrate 7 and (h) substrate 8.

Table 1  
Oxidation of alcohols catalyzed HPW(15%)/MCM41 in **IL3**



	Substrate	Product	Conversion (%)	Time (h)
1			99	2.5
2			96	2.5
3			95	2.5
4			94	2.5
5			90	3
6			93	3
7			98	2.5
8			96	2.5

strates, reaction media, etc. In this work, we focused on a series of MCM-41 supported photocatalysts ((*x*%) HPW/MCM-41) and their catalytic properties in ionic liquids. The main features of the catalytic properties we discussed here are the loading amount of HPW on MCM-41, the different type of ionic liquids and the comparative studies with traditional solvent.

### 3.1. Conversion and selectivity of the catalytic oxidation of alcohols

The results of the catalytic reactions carried out in **IL2** with HPW (30%)/MCM-41 as catalyst are listed in Table 1. All the studied alcohols were able to be selected converted to corresponding aldehydes or ketones at selectivity higher than 99% and conversions over 90% with reaction time less than 3 h. The effect of HPW loading amount on MCM-41, the effects of different ionic liquids and solvent effect were intensively

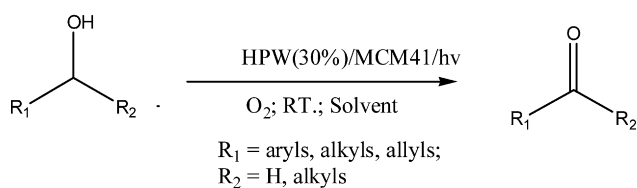
discussed. The results carried out with different variable conditions are shown in Table 2. The conversions of the alcohols (substrates 1–8) under different catalytic conditions are depicted in Fig. 2. It is easy to see that the conversions of the substrates to corresponding products varied with different reaction conditions.

### 3.2. Effect of HPW loading amount on MCM-41

In order to investigate the loading amount of HPW on MCM-41, we synthesized HPW and HPW (*x*%) /MCM-41, where *x*% is the respective HPW contents of 15, 30 and 50 wt%. Their properties have been listed in Table 3.

The catalytic property of HPW in **IL2** as a homogenous catalytic system was firstly investigated. All the studied alcohols were oxidized to corresponding aldehydes or ketones in 80–87% conversions, as shown in Table 2 and Fig. 3. To compare the cat-

Table 2  
Photocatalytic oxidation of alcohols with different variable conditions



Substrate	HPW				HPW(15%)/MCM41				HPW(30%)/MCM41				HPW(50%)/MCM41			
	CH <sub>3</sub> CN	IL1	IL2	IL3	CH <sub>3</sub> CN	IL1	IL2	IL3	CH <sub>3</sub> CN	IL1	IL2	IL3	CH <sub>3</sub> CN	IL1	IL2	IL3
1	75	85	87	84	90	95	97	94	91	97	99	96	88	93	94	92
2	73	82	84	82	87	92	94	91	88	95	96	93	85	90	90	89
3	70	82	83	81	82	88	92	90	83	92	95	92	80	86	89	88
4	71	78	80	80	80	85	91	86	81	88	94	88	78	83	88	84
5	70	78	81	80	78	83	87	87	78	85	90	90	77	82	85	84
6	71	80	82	81	79	84	88	84	80	88	93	87	76	81	85	82
7	73	82	84	83	84	88	96	90	85	91	98	92	81	85	95	87
8	70	78	80	79	80	84	93	88	82	87	96	90	78	82	90	85

Table 3  
Structural data of HPW, MCM-41 and HPW/MCM-41 catalysts

Samples	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (Å)	HPW phase
HPW	<10			Crystalline
HPW (15%)/MCM-41	1128	0.98	30.0	Amorphous
HPW (30%)/MCM-41	632	0.53	29.7	Amorphous
HPW (50%)/MCM-41	499	0.40	29.5	Amorphous
Si-MCM-41	1311	1.03	31.4	–

alytic properties of HPW and HPW (*x*%) /MCM-41 catalysts, where *x*% is the respective HPW content of 15, 30 and 50 wt%, catalytic reactions of the alcohols were conducted under similar reaction conditions with varying the loading amount of HPW on MCM-41. It is clear that all the conversions of the substrates catalyzed by HPW (*x*%) /MCM-41 catalysts were higher than those by the HPW homogenous catalyst. The average conversions of substrates were increased by 5–15%. With the loading amount of HPW increasing from 15 to 30%, the conversions of the substrates were increased, because more active sites were generated with the increase in the loading amount of HPW on MCM-41. However, with increasing loading amount of HPW from 30 to 50%, the conversions of the substrates were decreased. This may be due to the catalytic performance of the HPW (*x*%) /MCM-41 catalysts is not only related to the loading amount of HPW on

MCM-41, but also governed by the pore structure and surface area of the materials. As shown in Table 3, as the loading amount of HPW increased, the pore diameter of HPW (*x*%) /MCM-41 were not much affected, but the surface area and pore volume decreased dramatically. This might be because of a partial blockage of the monodimensional channels of MCM-41 by small aggregates of HPW, thus decreasing the accessibility of the active sites to the reactants, which is in agreement with the findings of Blasco et al. [15b]. The aggregation of HPW may be also the reason for the decrease in the surface area of HPW/MCM-41 with the increase in the HPW loading as we found before (see Table 3) [16c].

### 3.3. Solvent effects

In order to investigate solvent effects on the catalytic properties of the photocatalysts, we chose HPW (30%) /MCM-41. Results are depicted in Fig. 4. All the conversions in ILs were at least 5% higher than those in CH<sub>3</sub>CN. The overall conversions of most of the substrates were higher in IL2 than in other ILs. However, conversions of the substrates to corresponding products varied with substrates and ILs. This may be due to the facts that the properties of ionic liquids varied with different cationic and anionic parts. In the studied ILs, the alkyl part (IL2 and IL3), as well as anions (IL1), had significant influence on its physical and chemical properties, such as density, viscosity and solubility, especially solubility, which might affect the catalytic properties of the HPW (30%) /MCM-41.

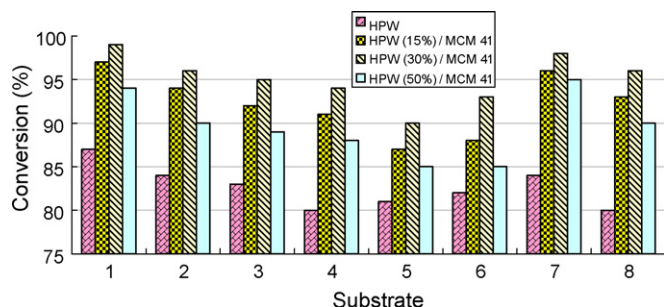


Fig. 3. Effect of loading amount of HPW on MCM-41 (reactions were carried out in IL2).

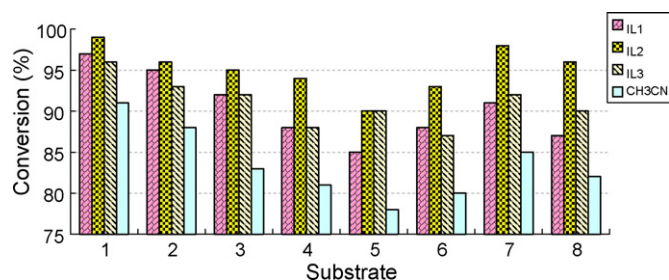


Fig. 4. Solvent effect on the catalytic activity of HPW(30%)/MCM-41.

#### 4. Conclusion

The selective oxidation of alcohols by a series of HPW/MCM-41 as photocatalysts with an enhanced activity in the presence of ionic liquids was studied. The loading amount of HPW on MCM-41 and the effects of different ionic liquids were shown in this work. The catalytic activity of HPW/MCM-41 was higher than that of HPW. The optimal loading amount of HPW in HPW/MCM-41 was 30%. The catalytic performance of HPW (30%)/MCM-41 in ILs was better than that in CH<sub>3</sub>CN. The HPW/MCM-41 systems were able to be used as photocatalysts for selective oxidation of alcohols. ILs have a strong favorable effect on the catalytic performance.

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