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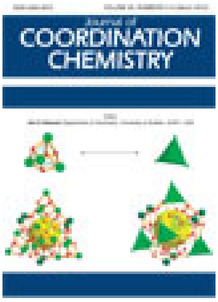

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Selective oxidation of alcohols to aldehydes using inorganic-organic hybrid catalyst based on zinc substituted polyoxometalate and ionic liquid

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Selective oxidation of alcohols to aldehydes using inorganic–organic hybrid catalyst based on zinc substituted polyoxometalate and ionic liquid

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Various organic–inorganic hybrid compounds, $[\mathrm{bmim}]_x[\mathrm{PW_{11}MO_{39}}]\cdot 3\mathrm{H_2O}$ {(bmim: 1-*n*-butyl-3-methylimidazolium) and [M = V(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II)]}, were prepared and characterized by elemental analysis, UV-Vis, FT-IR, and TGA. The synthesized hybrid compounds were used as catalysts in oxidation of various alcohols with hydrogen peroxide in acetonitrile. The effect of the transition metal on the catalytic activity was in the order, Zn > Fe > Ni > Cr > Co > V > Mn > Cu. In this catalytic system, the effects of other parameters such as the type of solvent, amount of oxidant and catalyst, and the temperature were also investigated. $[\mathrm{bmim}]_5[\mathrm{PW_{11}ZnO_{39}}]\cdot 3\mathrm{H_2O}$ was reused several times without loss of catalytic activity.

Keywords: Hybrid catalyst; Polyoxometalate; Ionic liquid; Oxidation; Alcohol; Aldehyde

1. Introduction

Selective oxidation of hydrocarbons with green oxidants is of importance in industrial chemistry because many petrochemical compounds are produced by these processes [1]. Oxidation of alcohols to carbonyl compounds is an important functional group transformation [2, 3]. Many inorganic oxidants such as pyridinium chlorochromate (PCC) [4], MnO_2 [5], pyridinium dichromate (PDC) [6], CrO_3 [7], H_2CrO_4 [8], CrO_2 [9], $KMnO_4$ [10], K_2FeO_4 [11], ClO_2 [12], H_5IO_6 [13], $NaIO_4$, and NaClO [14] have been employed for oxidation of alcohols. However, most of these oxidants are toxic, expensive, or hazardous. The best oxidants in oxidation reactions are molecular oxygen [15–19] and hydrogen peroxide [20–23]. Hydrogen peroxide is a very attractive, green, and clean oxidant for liquid phase oxidations, because in oxidation with hydrogen peroxide, water is the only by-product. This oxidant is much cheaper and safer than most other organic and inorganic oxidants. Therefore, the discovery of new

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environmentally friendly methods for selective oxidation of alcohols with hydrogen peroxide is an important goal in chemical synthesis.

Ionic liquids (ILs) are employed as green solvents [24], catalysts, and co-catalysts in organic reactions such as oxidation, reduction, alkylation, and condensation. [25]. Recently, ILs in immobilized and hybridized forms have been applied as catalysts [26].

Polyoxometalates (POMs) are metal-oxygen anionic clusters in which the chemical properties can be controlled by transition metal substitution and by changing the type of counter-cation [27]. Keggin structures, $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ ($X = P^{5+}$, Si^{4+}, Ge^{4+}, B^{3+} and $M = W^{6+}$ or Mo^{6+}) are the most investigated POMs. In Keggin structures, M can be substituted by other transition metals to form transition metal substituted Keggin type POMs (TMSPs) [28, 29]. Transition metal substituted polyoxometalates (TMSPs) have been reported as excellent catalysts in oxidation reactions [30].

The design and synthesis of POM-based hybrids is an area of research in materials chemistry because these materials have roles in catalysis, molecular magnetism, optics, electronic versatility, photochemistry, and medicine [31–37]. Also, in POM-based hybrid materials, the large metal oxide anionic frameworks can react electrostatically with room temperature ILs to form new hybrid composite systems [38–40].

In continuation of our studies on the oxidation of organic compounds [41–47], herein, we report a simple, efficient, and green method for selective oxidation of primary and secondary alcohols with hydrogen peroxide catalyzed by $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ (scheme 1).

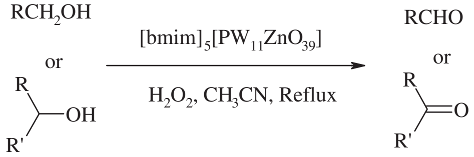
2. Experimental

2.1. *General*

All chemicals and reagents were purchased from Fluka or Merck chemical companies and used without purification. The UV-Vis spectra were recorded on a Shimadzu-160 UV-Vis spectrophotometer. FT-IR spectra (400–4000 cm^{-1}) were recorded as KBr pellets using a Shimadzu Corporation spectrometer. Gas chromatography (GC) experiments were performed on a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20M. In GC experiments, *n*-decane was used as internal standard and yields were determined by using peak area. Thermogravimetric analysis (TGA) of the catalyst was carried out on a Mettler TA4000 instrument.

2.2. *Preparation of hybrid catalysts*

$[PW_{11}MO_{39}]^{(n-m)-}$ was prepared according to the literature method [48]. An aqueous solution of $[PW_{11}MO_{39}]^{(n-m)-}$ was prepared by mixing Na_2HPO_4 (9.1 mmol),



Scheme 1. Oxidation of alcohols with H_2O_2 catalyzed $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$.

$Na_2WO_4 \cdot 2H_2O$ (100 mmol) and the nitrate salt of M [M = V(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II)] (12 mmol) in 200 mL of water and adjusting pH to 4.8. An aqueous solution of $[bmim]NO_3$ (45 mmol) (20 mL) was added dropwise, with stirring, at room temperature and the resulting solid was filtered.

2.3. *General procedure for oxidation of alcohols*

To a solution of alcohol (1 mmol) and $[bmim]_x[PW_{11}MO_{39}] \cdot 3H_2O$ (0.05 mmol) in acetonitrile (3 mL) H_2O_2 (30%, 1 mL, 10 mmol) was added. The reaction mixture was stirred under reflux and the progress of the reaction was monitored by thin layer chromatography (TLC) or GC. After completion of the reaction, the reaction mixture was cooled to room temperature, the solvent was evaporated and *n*-hexane (10 mL) was added. The catalyst was filtered and washed with *n*-hexane. The solvent was evaporated and the pure product was obtained by chromatography on a short column of silica gel (20 cm length, 1 cm diameter, eluent 1 : 8 ethyl acetate: *n*-hexane; the product separated before the alcohol).

3. Results and discussion

3.1. *Characterization of the catalysts*

The nitrate anion in $[bmim]NO_3$ was replaced with the substituted bulky anion $[PW_{11}MO_{39}]^{n-}$ and the organic–inorganic hybrid material was prepared. Organic–inorganic hybrid catalysts were characterized by elemental analysis, FT-IR, and UV-Vis spectroscopic methods.

The most informative data for studying the catalyst structures were obtained by FT-IR spectroscopy. The FT-IR spectra of 1-butyl-3-methylimidazolium nitrate, $H_3PW_{12}O_{40} \cdot nH_2O$ and $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ are shown in "Supplementary material" and the major assignments are given in table 1. The FT-IR spectra clearly show the characteristic bands of $[bmim]^+$ (1100–1600 and 2700–3200 cm^{-1}) and $PW_{12}O_{40}^{3-}$ (450–1100 cm^{-1}). The vibrations at 1650 and 3500 cm^{-1} are assigned to water in the $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ hybrid catalyst [49].

UV-Vis spectra of $[bmim]NO_3$ and $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ are shown in "Supplementary material." The heteropoly acids are generally characterized by oxygen-to-metal (O → M) charge transfer bands which appear in the UV region below 400 nm [50]. When materials based on heteropoly acids are irradiated with UV light, electrons are excited from the low-energy electronic states (mainly oxygen 2p orbitals in heteropoly anions) to high-energy states (mainly metal d orbitals). UV-Vis spectroscopy, in the diffuse reflectance mode, was employed for characterization of this catalyst. The UV-Vis spectrum of $H_3PW_{12}O_{40}$ is shown in "Supplementary material." An absorption is present at 255 nm due to charge transfer transitions in the Keggin units. In the UV-Vis spectrum of $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$, this absorption appears at 251 nm (Supplementary material).

The thermal stability of $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ was monitored by TGA which determines the presence of water and also the stability of the catalyst. The effect of thermal treatment on $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ is shown in

Table 1. IR bands of [bmim]NO_3, $H_3PW_{12}O_{40}$, and $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$.

	Wavenumber (cm^{-1})		
Vibration	$[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$	$H_3PW_{12}O_{40}$	[bmim]NO_3
Water in the material	3437	3415	3460
Imidazole ring ν(C–H)	3145, 3103	–	3154, 3090
Aliphatic ν(C–H)	2959, 2931, 2870	–	2963, 2936, 2882
Imidazole ν(ring)	1572, 1566	–	1573, 1563
Imidazole H–C–C and H–C–N bending	1165		1169
ν(P–O)	1065	1079	–
ν(W–O_t)	980	987	
ν(W–O_c–W)	892	886	
ν(W–O_e–W)	807	810	–
ν(Zn–O)	946	–	–

Vibrational frequencies modes of both catalysts and parent components.

"Supplementary material." The TG-DTG curve shows that the $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ decomposed at 350–500°C and the water molecules are lost below 200°C. The results indicate that three hydrated water molecules are present in the catalyst.

3.2. *The effect of TMSPs on oxidation of benzyl alcohol*

In order to find the best catalytic system, the oxidation of benzyl alcohol with H_2O_2 as a model reaction was studied under reflux in the presence of various TMSPs. The results are listed in table 2. $H_3PW_{12}O_{40} \cdot 3H_2O$ showed low activity (table 2, entry 1), but in the presence of $[bmim]_3[PW_{12}O_{40}] \cdot 3H_2O$, 49% of benzaldehyde was detected in the reaction mixture (table 2, entry 2). These results show that both 1-butyl-3-methyl imidazolium and the POM have essential roles in the oxidation. The catalytic activity of various TMSPs was also checked in oxidation of benzyl alcohol with H_2O_2. The results showed the catalytic activities were in the order, $Zn > Fe > Ni > Cr > Co > V > Mn > Cu$. For Mn, Fe, Co, and Cu, peroxo intermediates lead to the homolytic cleavage of the O–O bond and produce radicals [51]. Addition of acrylonitrile as radical scavenger confirmed this and reduced amounts of products. For Zn compound, acrylonitrile has no significant effect, indicating the preferred reaction path is heterolytic cleavage of the O–O bond. Among the IL–POM hybrid catalysts containing various transition metals, $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ showed the highest yield (100%, 1.15 h) in oxidation of benzyl alcohol (table 2, entry 3). These observations show that the nature of transition metal ion also has a crucial role in the catalytic activity of these catalysts for oxidation of benzyl alcohol. Sodium and ammonium salts of POM showed low catalytic activity in oxidation reactions (table 2, entries 12 and 13). It seems that a synergistic effect between IL and POM due to similar size increased the catalytic activity. Also the presence of IL improved the stability and solubility of the catalyst in the organic solvent. Therefore, $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ was chosen as the best catalyst. In the absence of catalyst only 5% benzaldehyde was obtained after 75 min (table 2, entry 13), showing that the presence of catalyst is essential in this oxidation.

Table 2. Oxidation of benzyl alcohol using H_2O_2 catalyzed by various catalysts $[bmim]_x[PW_{11}MO_y] \cdot 3H_2O$ under reflux.[a]

Entry	Catalyst	Yield (%)[b] after 75 min
1	$H_3PW_{12}O_{40} \cdot 3H_2O$	10
2	$[bmim]_3[PW_{12}O_{40}] \cdot 3H_2O$	49
3	$[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$	100
4	$[bmim]_4[PW_{11}FeO_{39}] \cdot 3H_2O$	64
5	$[bmim]_5[PW_{11}NiO_{39}] \cdot 3H_2O$	59
6	$[bmim]_4[PW_{11}CrO_{39}] \cdot 3H_2O$	34
7	$[bmim]_5[PW_{11}CoO_{39}] \cdot 3H_2O$	20
8	$[bmim]_5[PW_{11}MnO_{39}] \cdot 3H_2O$	8
9	$[bmim]_4[PW_{11}VO_{40}] \cdot 3H_2O$	6
10	$[bmim]_5[PW_{11}CuO_{39}] \cdot 3H_2O$	5
11	$Na_5[PW_{11}ZnO_{39}] \cdot 3H_2O$	7
12	$[NH_4]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$	8
13	No catalyst	5

[a] Reaction conditions: benzyl alcohol (1 mmol), H_2O_2 (10 mmol), catalyst (0.05 mmol), CH_3CN (3 mL).
[b] GC yield based on the starting alcohol.

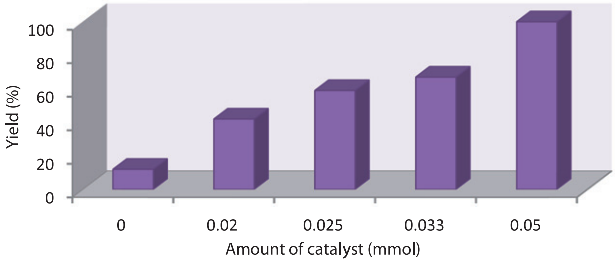


Figure 1. The effect of $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ amount on oxidation of benzyl alcohol for 1.25 h, reaction conditions: 1 mmol benzyl alcohol, 10 mmol H_2O_2, 3 mL acetonitrile, reflux.

3.3. *Effect of catalyst amount on the oxidation of benzyl alcohol*

To optimize amounts of $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$, various amounts of catalyst were used for oxidation of benzyl alcohol. As shown in figure 1, the best result was obtained in the presence of 0.05 mmol of $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ hybrid catalyst under reflux after 1.25 h (figure 1).

3.4. *Effect of oxidant on the oxidation of benzyl alcohol*

The effect of different oxidants such as Urea-H_2O_2 (UHP), *tert*-BuOOH and H_2O_2 on the catalytic activity of $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ in the oxidation of benzyl alcohol was also studied. The conversion with UHP and *tert*-BuOOH in the presence of $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ was only a trace even after 6 h, while in the presence of H_2O_2 the reaction was complete after just 1.25 h. Therefore, hydrogen peroxide was chosen as the best oxidant.

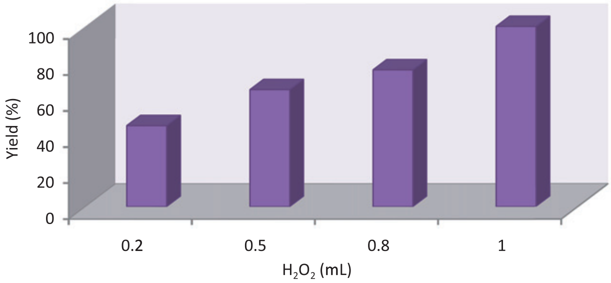


Figure 2. The effect of oxidant amount on oxidation of benzyl alcohol catalyzed by $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ for 1.25 h, reaction conditions: 1 mmol benzyl alcohol, 3 mL acetonitrile, 0.05 mmol $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ catalyst, reflux.

The effect of H_2O_2 (30%) amount on the oxidation of benzyl alcohol was also studied in the same reaction. The highest yield was obtained with 1 mL (10 mmol) of H_2O_2 (figure 2). Therefore, 1 mL (10 mmol) H_2O_2 (30%) was found to be optimal in these oxidation reactions.

3.5. *Effect of temperature on the oxidation of benzyl alcohol*

For finding the optimum temperature in oxidation of benzyl alcohol, the reaction was performed at different temperatures. The yield of the product was very low at room temperature even after 6 h and the highest yield was obtained under reflux; therefore, the reactions were carried out under reflux conditions.

3.6. *Effect of solvent*

As shown in figure 3, among the various solvents tested, CH_3CN was best for oxidation with higher catalytic activity. The higher catalytic activity in acetonitrile can be attributed to polarity and better solubility of the catalyst. In CH_2Cl_2, $CHCl_3$, and EtOAc lower catalytic activities were observed. The product yield observed for H_2O was 90% after 4 h. Although H_2O is a green solvent, the products required longer reaction times compared to acetonitrile and therefore acetonitrile was used as solvent. There was also lower solubility of the substrates and products in water. Our studies in this field continue.

3.7. *Oxidation of alcohols with H_2O_2 catalyzed by $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$*

To study the scope and generality of this procedure, oxidation of different alcohols was studied under the optimized reaction conditions with H_2O_2 in the presence of $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ (table 3, entries 1–19). The reaction times and yields of products are shown in table 3. For benzylic alcohols, the nature of substituents (electron-withdrawing or electron-donating) has a significant effect on product yield.

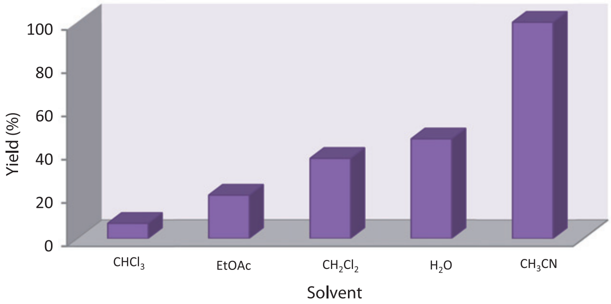


Figure 3. The effect of solvent on the oxidation of benzyl alcohol catalyzed by $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ for 1.25 h, reaction conditions: 1 mmol benzyl alcohols, 10 mmol H_2O_2, 0.05 mmol $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ catalyst, reflux.

For example, 4-methoxybenzyl alcohol was converted into its corresponding aldehyde in excellent yield (100%) after 0.5 h, while for 2-fluorobenzyl alcohol only 47% of its corresponding aldehyde was produced after 2 h. Compared to benzylic alcohols, aliphatic alcohols showed relatively low reactivity toward oxidation. The 3-pyridylmethanol as a heterocyclic alcohol was oxidized to its corresponding aldehyde in excellent yields after only 0.5 h. The selectivity of this method was also investigated. When a mixture of 1-heptanol and benzyl alcohol was subjected to oxidation, benzaldehyde was produced in 97% yield and only 10% of 1-heptanal was detected. When a mixture of cyclohexanol and benzyl alcohol was subjected to oxidation, only benzaldehyde was detected in 100% yield (table 3, entries 20, 21). Such selectivity can be considered as a useful practical achievement in oxidation of alcohols. These observations clearly reveal that this method can be applied for chemoselective oxidation of benzylic alcohols in the presence of primary and secondary alcohols. In order to show the efficiency of this catalyst, the oxidation of benzyl alcohol was compared with several other recorded catalytic systems (table 4) [52–56], showing that our reported method is superior in terms of reaction time and/or product yield.

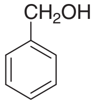
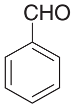
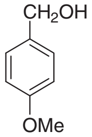
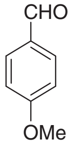
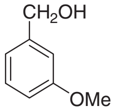
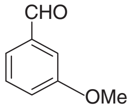
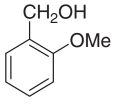
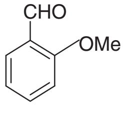
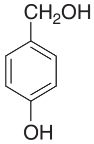
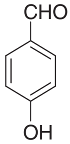
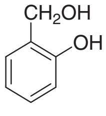
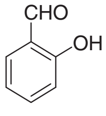
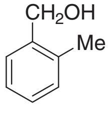
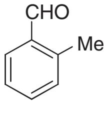
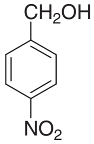
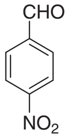
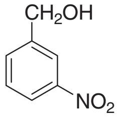
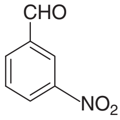
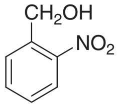
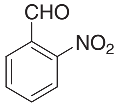
3.8. *Recovery of $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ catalyst*

The recyclability of the catalyst was tested in the catalytic oxidation of benzyl alcohol. After 1.25 h the catalyst was filtered, washed with *n*-hexane, and dried at room temperature. This catalyst was used in successive runs under similar conditions. The results in table 5 indicate that $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ can be recycled four consecutive times without a significant decrease in its activity.

4. Conclusion

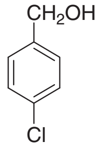
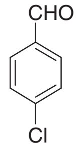
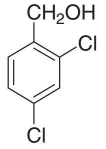
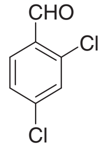
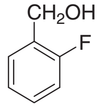
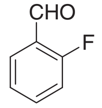
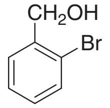
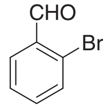
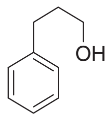
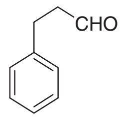
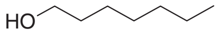
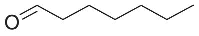
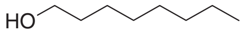
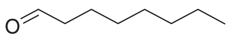
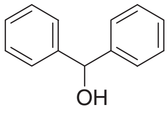
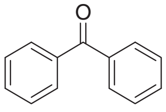
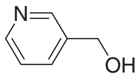
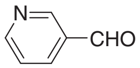
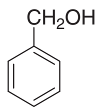
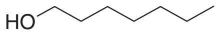
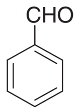
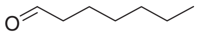
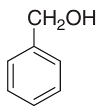
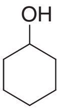
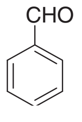
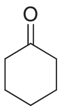
The $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ catalyst was prepared by the reaction of 1-butyl-3-methylimidazolium nitrate and zinc substituted POM and characterized by elemental

Table 3. Selective oxidation of alcohols using H_2O_2 catalyzed by $[bmim]_5[PW_{11}ZnO_{39}]\cdot 3H_2O$ hybrid catalyst.[a]

Entry	Substrate	Product	Time (h)	Yield (%)[b]
1			1.25	100
2			0.5	100
3			2	98
4			1	100
5			2	98
6			2.5	100
7			3	100
8			3.5	98
9			2	92
10			3	75

(*Continued*)

Table 3. Continued.

Entry	Substrate	Product	Time (h)	Yield (%)^b
11			4	100
12			3	74
13			2	47
14			4	90
15			3.5	43
16			6	56
17			4	26
18			0.25	70
19			0.5	100
20^c	 	 (1)  (2)	1.25	(1) 97 (2) 10
21^c	 	 (1)  (2)	1.25	(1) 100 (2) 0

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[a] Reaction conditions: alcohol (1 mmol), H_2O_2 (10 mmol), $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ (0.05 mmol), CH_3CN (3 mL).

[b] GC yields based on the starting alcohol.

[c] Reaction conditions: benzyl alcohol (1 mmol), aliphatic alcohol (1 mmol), H_2O_2 (10 mmol), $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ (0.05 mmol), CH_3CN (3 mL).

Table 4. Comparison of results on the oxidation of benzyl alcohol catalyzed by $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ with several other recorded catalytic systems.

Entry	Oxidant	Catalyst	Time (min)	Yield (%)	Ref.
1	H_2O_2	$[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$	75	100	–
2	H_2O_2	$Na_6[SiW_{11}ZnH_2O_{40}] \cdot 12H_2O$	120	100	[52]
3	H_2O_2	$[(C_{18}H_{37})_2(CH_3)_2N]_7[PW_{11}O_{39}]$	420	56	[53]
4	H_2O_2	$Na_9[SbW_9O_{33}]$	120	94	[54]
5	H_2O_2	$H_3PMo_{12}O_{40}$	300	84	[55]
6	O_2	$H_3PW_{12}O_{40}/ZrO_2$	240	81	[56]

Table 5. The results of $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ catalyst recovery in the oxidation of benzyl alcohol with hydrogen peroxide at reflux.[a]

Run	Conversion (%)[b]
1	100
2	100
3	97
4	97

[a] Reaction conditions: benzyl alcohol (1 mmol), H_2O_2 (10 mmol), $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$ (0.05 mmol), acetonitrile (3 mL).
[b] GC yield.

analysis, TGA, and UV-Vis and FT-IR spectroscopic methods. The catalytic activity of the prepared catalyst was investigated in oxidation of alcohols with hydrogen peroxide. This catalytic system was used as a selective, recyclable, and efficient catalyst for alcohol oxidation.

Acknowledgments

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