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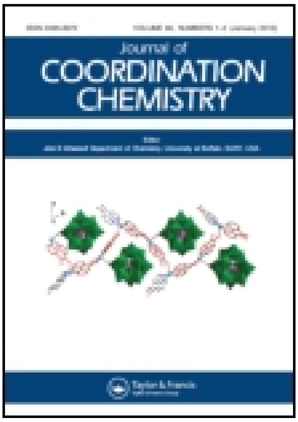

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Green and efficient oxidation of benzylic alcohols with hydrogen peroxide catalyzed by an inorganic-organic hybrid catalyst

Zahra Nadealian [a] , Valiollah Mirkhani [a] , Bahram Yadollahi [a] , Majid Moghadam [a] , Shahram Tangestaninejad [a] & Iraj Mohammadpoor-Baltork [a]

[a] Department of Chemistry , Catalysis DivisionUniversity of Isfahan , Isfahan , Iran

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Green and efficient oxidation of benzylic alcohols with hydrogen peroxide catalyzed by an inorganic–organic hybrid catalyst

ZAHRA NADEALIAN, VALIOLLAH MIRKHANI*, BAHRAM YADOLLAHI*, MAJID MOGHADAM*, SHAHRAM TANGESTANINEJAD and
IRAJ MOHAMMADPOOR-BALTORK

Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan, Iran

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Inorganic–organic hybrid catalysts **1**-POM(M) were prepared by electrostatic interaction between transition metal-substituted polyoxometalates, {$[PW_{11}MO_{39}]^{4-}$ [M = Cr(III), Fe(III)], $[PW_{11}MO_{39}]^{5-}$, [M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)], $[PW_{11}VO_{40}]^{4-}$}, and branched organic polyammonium, (*tris*[2-(dimethylammonium)ethyl]-1,3,5-benzenetricarboxylate), and characterized by elemental analyses, UV–vis and FT IR spectroscopic techniques, XRD, SEM, and Thermogravimetric-Differential thermogravimetric analyses. The hybrid material **1**-POM(Zn) was an efficient and selective heterogeneous catalyst in the oxidation of benzylic alcohols to their corresponding carbonyl compounds with hydrogen peroxide. The catalyst was reused several times without significant loss of catalytic activity.

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

1. Introduction

Inorganic–organic hybrid materials have found many applications in chemistry and materials science [1]. Based on the structural distinction, Sanchez and Ribot classified inorganic–organic hybrid materials into two classes: Class I corresponds to hybrid systems in which weak interactions such as van der Waals forces, hydrogen bonds, or electrostatic interactions are created between organic and inorganic components and Class II corresponds to hybrid organic–inorganic compounds where both organic and inorganic components are bonded through strong covalent bonds [2]. Synthesis and structural characterization of new hybrid materials are of interest due to their possible applications in catalysis, molecular magnetism and optics, and their electronic versatility and topological diversity [3–5].

The main disadvantage of homogeneous catalysts is their instability in oxidation media and difficulty in recovery, which limit the practical applications of homogeneous catalysts in both synthetic chemistry and industrial processes. Therefore, linking homogeneous

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*Corresponding authors. Email: mirkhani@sci.ui.ac.ir (V. Mirkhani); yadollahi@sci.ui.ac.ir (B. Yadollahi); moghadamm@sci.ui.ac.ir (M. Moghadam) catalysts with organic structures can provide hybrid catalysts, which are easier to handle, and may exhibit improved selectivity and activities [6]. Several approaches to dendritic catalysis and dendrimers in catalysis have been reported [7–9]. Dendrimers have advantages compared with homogeneous and heterogeneous catalysis as it is possible to change the shape, size, structure, and solubility of dendrimers and metallodendrimers, and to locate the catalytic sites at the core or periphery [10]. Organometallic, inorganic, or organic catalysts [11] supported on inorganic polymers (such as silica) or organic polymers (such as polystyrene) have been investigated [12], but dendrimers now suggest better control of the shape, number, and structure of the catalytic sites and their microenvironment.

Polyoxometalates (POMs) are transition metal oxygen anion clusters that exhibit a wide range of molecular sizes and compositions [13]. POMs have been employed as important inorganic building blocks for constructing hybrid materials with various organic molecules [14–17]. Transition metal-substituted polyoxometalates are good catalysts for oxidation reactions. They exhibit advantages, because their catalytic properties can be tuned by changing the identity of charge-compensating countercations, heteroatoms, and framework metals [18–20].

Selective oxidation of alcohols to their corresponding carbonyl compounds plays an important role in organic synthesis and many biological reactions, providing key biological intermediates and valuable pharmaceuticals [21, 22]. Many oxidations of this type have been reported using stoichiometric amounts of oxidizing organic and inorganic reagents such as K_2FeO_4 [23], Pyridinium chlorochromate [24], MnO_2 [25], CrO_3 [26], CrO_2 [27], $KMnO_4$ [28, 29], and ClO_2 [30] with drawbacks such as high cost, waste by-products, and serious environmental issues. Hence, the quest for effective catalytic systems that use clean, inexpensive oxidants such as oxygen and hydrogen peroxide for the conversion of alcohols to carbonyl compounds on an industrial scale remains an important challenge [20, 31–34].

In continuation of our interest in homogeneous and heterogeneous catalysts in various oxidation reactions [35–38], in this paper we wish to report the preparation of hybrid catalysts **1**-POM(M) [M = Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), V(IV)] based on the electrostatic interaction between Keggin-type POMs and branched organic polyammonium salt, (*tris*[2-(dimethylammonium)ethyl]-1,3,5-benzenetricarboxylate), and their application as heterogeneous catalysts in efficient and selective oxidation of alcohols to their corresponding carbonyl compounds.

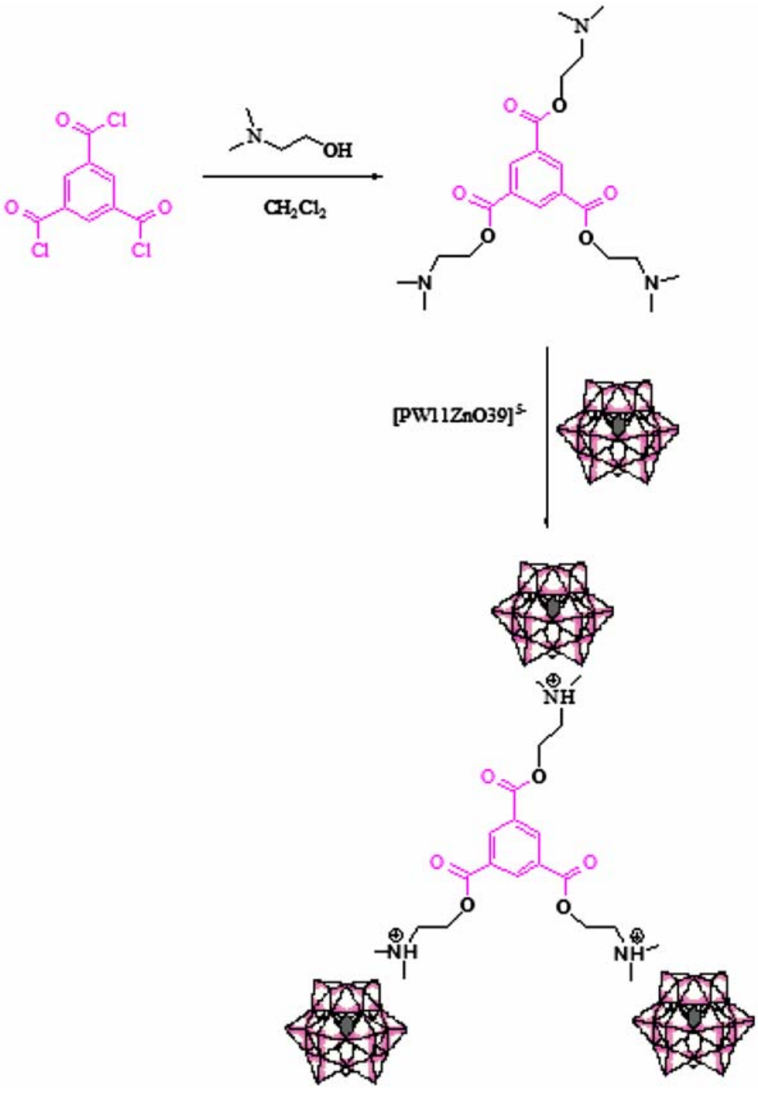
2. Experimental

2.1. *Materials and methods*

All chemicals and reagents were obtained from Fluka or Merck chemical companies and used without purification. UV–Vis spectra (200–800 nm at 25 °C) were recorded on a Shimadzu-160 UV–Vis spectrophotometer. FT IR spectra (400–4000 cm^{-1}) were recorded as KBr pellets at 25 °C using a JASCO 6300 spectrometer. Gas chromatography (GC) experiments were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 M. In the GC experiments, *n*-decane was used as internal standard and the yields were determined by using peak area. Powder X-ray diffraction patterns were obtained on a D_8 Advanced Bruker using Cu K_α radiation ($2\theta = 5$–60°). Thermogravimetric analyses were achieved on a Mettler TA4000 thermobalance instrument.

2.2. *Preparation of benzene-1,3,5-tricarboxylic acid tris(2-dimethylaminoethyl)ester 1*

Benzene-1,3,5-tricarboxylic acid tris(2-dimethylaminoethyl)ester **1** was synthesized from 1,3,5-benzenetricarbonyl trichloride and *N*,*N*-dimethylethanolamine in CH_2Cl_2 (Scheme 1). The organic layer was separated, diluted with CH_2Cl_2, washed with water, and concentrated under vacuum. The oil product was dried under vacuum and used in the next step without purification [39]. ^1H NMR ($CDCl_3$): $\delta = 2.16$ (18H, s, 6CH_3), 2.56 (6H, t, $^3J_{HH} = 5.6$ Hz, 3CH_2), 4.29 (6 H, t, $^3J_{HH} = 5.6$ Hz, 3CH_2), 8.65 (3 H, s, 3CH_{arom}) ppm. FT IR (KBr) $\nu = 3021$, 2962, 2597, 2479, 2128, 1727, 1608, 1468, 1406, 1367, 1321, 1233, 1143, 1080, 925, 885, 738, 665, 508 cm^{-1}.



Scheme 1. Preparation of hybrid catalyst **1**-POM(Zn).

2.3. *Preparation of hybrid catalyst 1-POM(M)*

The anions including $\{[PW_{11}MO_{39}]^{4-}$ [M = Cr(III), Fe(III)], $[PW_{11}MO_{39}]^{5-}$ [M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)], and $[PW_{11}VO_{40}]^{4-}\}$ were prepared by mixing Na_2HPO_4, $Na_2WO_4{\cdot}2H_2O$, and the nitrate salt of M in water at pH = 4.8 [40]. The synthesized benzene-1,3,5-tricarboxylic acid tris(2-dimethylaminoethyl)ester **1** was added dropwise to this solution with stirring at room temperature. The mixture was left for 2 h to complete precipitation and then the solid was filtered. The hybrid compounds **1**-POM(M) were thoroughly washed with ethanol and diethyl ether and dried under vacuum.

2.4. *Typical procedure for oxidation of alcohols*

In a typical reaction, to a mixture of benzyl alcohol (1 mmol, 108 mg) and hybrid compound **1**-POM(Zn) (0.05 mmol) in acetonitrile (3 mL), aqueous H_2O_2 30% (1 mL) was added. The reaction mixture was stirred in a preheated oil bath at reflux and the progress of the reaction was monitored by TLC or GC. After completion of the reaction, the mixture was cooled to room temperature and the catalyst was filtered, washed with *n*-hexane, and dried at room temperature to recover the catalyst. The solvent was evaporated and the pure product was obtained by chromatography on a short column of silica gel.

3. Results and discussion

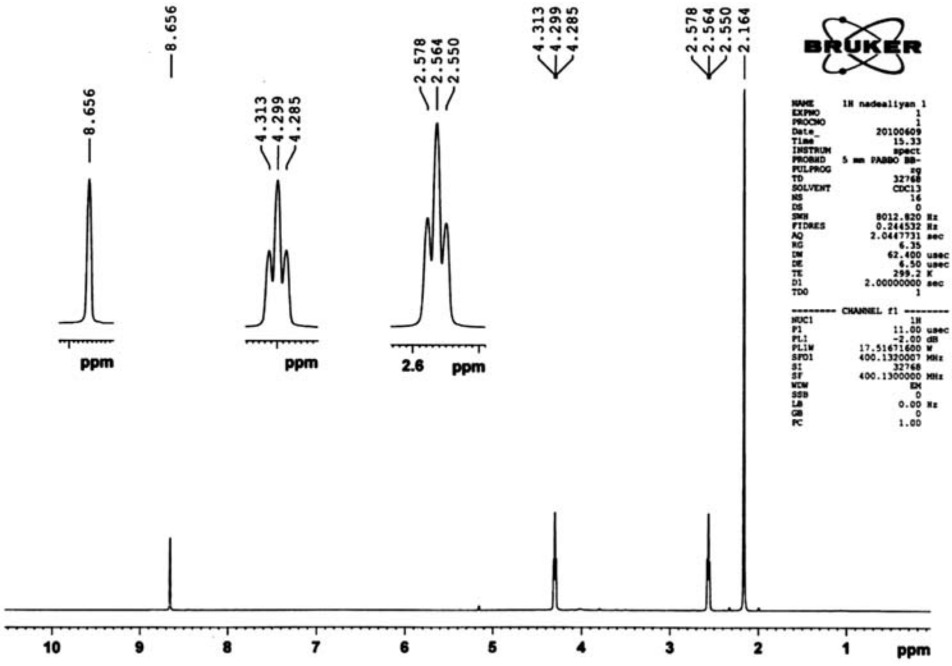
3.1. *Characterization of the hybrid catalyst 1-POM(Zn)*

First, benzene-1,3,5-tricarboxylic acid tris(2-dimethylaminoethyl)ester **1** as the organic building block in the hybrid catalyst was synthesized and characterized as reported [39]. The corresponding ^1H NMR (figure 1) and FT IR spectra (Supplemental material.docx) confirmed the synthesis of this branched organic compound.

Then, the hybrid catalysts **1**-POM(M) were synthesized by electrostatic interaction between transition metal-substituted POMs, $[PW_{11}MO_{39\ \mathrm{or}\ 40}]^{n-}$ [M = Cr(III), Mn(II), Fe (III), Co(II), Ni(II), Cu(II), Zn(II), V(IV)], and branched organic compound **1**.

The hybrid catalyst **1**-POM(Zn) was characterized by FT IR and diffuse reflectance UV–Vis spectroscopic techniques, SEM, XRD, and Thermogravimetric-Differential thermogravimetric (TG/DTG) analysis. The FT IR spectra of the hybrid catalyst **1**-POM(Zn) in the range 700–1100 cm^{-1} showed absorptions at 1085, 1052, 951, 884, and 808 cm^{-1}, which correspond to the five typical skeletal vibrations of the oxoanion structure. These peaks could be attributed to ν(P–O), ν(W–O_t), ν(Zn–O), ν(W–O_c–W), and ν(W–O_e–W), respectively. Stretching vibrations of the branched organic polyammonium structure were present at 3074, 2735, 2473, 1788, 1730, 1654, 1465, 1369, 1240, and 1154 cm^{-1}. These observations indicate the presence of a organic block in an inorganic–organic hybrid catalyst structure (Supplementary material).

The solid UV–Vis spectrum of inorganic–organic hybrid catalyst **1**-POM(Zn) is 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 [41]. The lowest energy electronic transition at 259 nm was assigned to a charge-transfer transition from the oxygen p-type non-bonding Highest Occupied Molecular Orbital to the tungsten d-type Lowest Unoccupied Molecular Orbital.



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TE                   299.2 K
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TD0                      1

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SI                   32768
SF             400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
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Figure 1. ^{1}H NMR spectrum of benzene-1,3,5-tricarboxylic acid tris(2-dimethylaminoethyl)ester **1**.

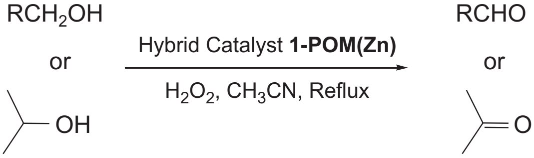
Thermogravimetric analysis performed up to 600 °C is shown in Supplementary material. Decomposition of the title compound showed a big endothermic peak centered at 400 °C, which was attributed to the transformation of **1**-POM(Zn) to $PW_{11}Zn$.

The powder XRD pattern of **1**-POM(Zn) is in agreement with the XRD pattern of $Na_5[PW_{11}ZnO_{39}]\cdot xH_2O$, indicating that the hybrid-prepared catalyst is well ordered (Supplementary material). The SEM images show morphology of the hybrid catalyst **1**-POM (Zn) (Supplementary material). The particles are aggregated and have different shapes and sizes.

According to the TGA curves, weight loss corresponding to the organic part is 23.85% and the amount of inorganic part is 66.64% (the remaining amount is related to waters in the structure of catalyst). The molecular weights are 423.24 and 2742.71 g/mol for organic and inorganic parts, respectively. Therefore, the molar ratio of organic to inorganic part is 7 to 3. The amount of Zn in the mesoporous catalyst structure, determined by ICP analysis, confirmed the proposed structure.

3.2. *Oxidation of alcohols with H_2O_2 catalyzed by hybrid catalysts, 1-POM(M)*

In order to find the best catalytic system, the oxidation of benzyl alcohol with hydrogen peroxide as a model reaction (Scheme 2) was studied under reflux in the presence of various hybrid catalyst **1**-POM(M) [M = Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), V(IV)]. The results are listed in table 1. The catalytic activity of **1**-POM(Zn) is higher than the other hybrid catalysts. Thermal and chemical stability, and redox and acidic properties of these hybrid catalysts could be controlled at the atomic or molecular levels by changing



Scheme 2. Oxidation of alcohols by hybrid catalyst **1**-POM(Zn).

Table 1. Oxidation of benzyl alcohol using H_2O_2 catalyzed by various hybrid catalysts **1**-POM(M).[a]

Entry	Catalyst	Conversion (%)[b] after 4.5 h
1	–	7
2	$[NH_4]_5[PW_{11}ZnO_{39}]\cdot 3H_2O$	34
3	**1**-POM(V)	10
4	**1**-POM(Cr)	59
5	**1**-POM(Mn)	20
6	**1**-POM(Fe)	79
7	**1**-POM(Co)	41
8	**1**-POM(Ni)	68
9	**1**-POM(Cu)	8
10	**1**-POM(Zn)	100
11	$Na_3PW_{12}O_{40}$	23

[a] Reaction conditions: benzyl alcohol (1 mmol), H_2O_2 (1 mL), catalyst (0.05 mmol), CH_3CN (3 mL), reflux $t = 4.5$ h.
[b] GC yield.

the basic element without affecting the Keggin primary structure [42]. For Mn, Fe, Co, and Cu, peroxo-intermediates lead to homolytic cleavage of the O–O bond and produce radicals [43]. Addition of acrylonitrile or 2,6-di-*tert*-butylphenol as radical scavengers confirmed this point and the amounts of the products reduced considerably. In the case of Zn compound, acrylonitrile or 2,6-di-*tert*-butylphenol has no significant effect. The preferred reaction path is heterolytic cleavage of the O–O bond [43]. Therefore, **1**-POM(Zn) was chosen as the catalyst in this study. In the absence of the catalyst, only 7% of benzaldehyde was obtained after 4.5 h (table 1, entry 1); in the presence of non-metal-substituted POM ($Na_3PW_{12}O_{40}$), only 23% of benzaldehyde was produced (table 1, entry 11).

To optimize the amounts of catalyst, different amounts of **1**-POM(Zn) were used in the oxidation of benzyl alcohol. As shown in figure 2, when the reaction was carried out in the presence of 0.05 mmol of catalyst, the best result was obtained under reflux after 4.5 h and benzaldehyde was produced in 100% yield. Blank experiment under the same conditions in the absence of the catalyst was also performed and only 7% of the product was detected in the reaction mixture after 4.5 h.

Then, different oxidants in the oxidation of benzyl alcohol were studied, $NaIO_4$, NaOCl, urea–H_2O_2 (UHP), *tert*-BuOOH, and H_2O_2. The results, summarized in table 2, showed when hydrogen peroxide (30%) was used as the oxygen source, higher conversion was obtained.

In order to find the optimized amount of hydrogen peroxide, oxidation of benzyl alcohol with different amounts of H_2O_2 30% (0.2, 0.5, 0.8, and 1 mL) was examined. As shown in figure 3, when the reaction was carried out in the presence of 1 mL 30% H_2O_2, higher

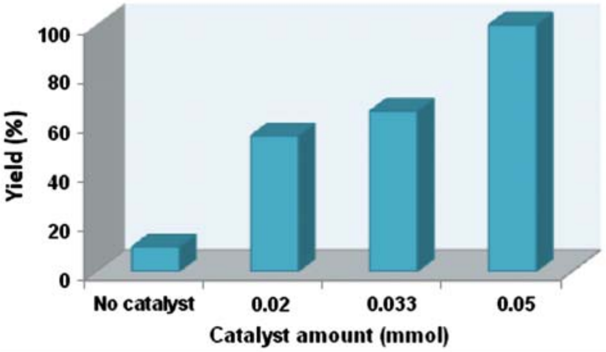


Figure 2. The effect of amount of hybrid catalyst **1**-POM(Zn) on the oxidation of benzyl alcohol.

Table 2. The effect of oxidant on the oxidation of benzyl alcohol catalyzed by **1**-POM(Zn).[a]

Entry	Oxidant	Solvent	Yield (%)[b]
1	H_2O_2	CH_3CN	100
2	*tert*-BuOOH	CH_3CN	48
3	$NaIO_4$	CH_3CN	12
4	H_2O_2/Urea	CH_3CN	22
5	No oxidant	CH_3CN	12

[a] Reaction conditions: benzyl alcohol (1 mmol), oxidant (10 mmol), catalyst **1**-POM(Zn) (0.05 mmol), CH_3CN (3 mL), reflux, $t = 4.5$ h.
[b] GC yield.

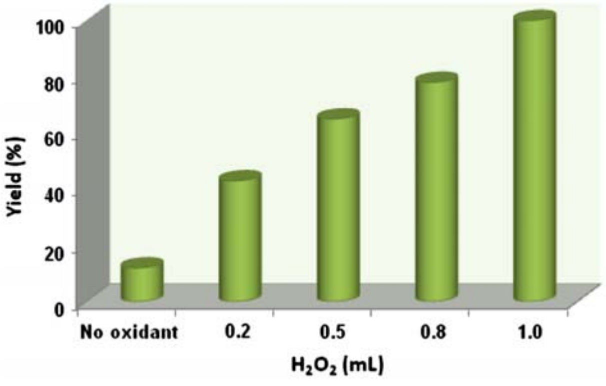
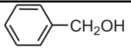
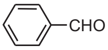
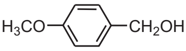
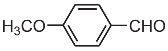
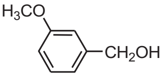
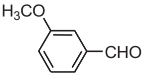
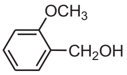
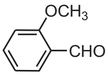
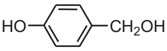
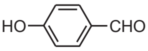
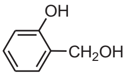
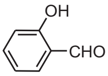
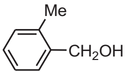
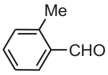
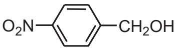
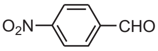
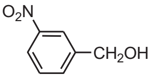
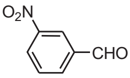
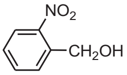
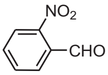
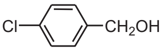
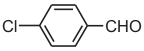
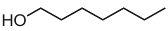
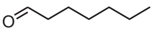
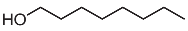
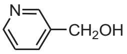
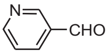
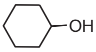
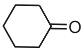


Figure 3. The effect of oxidant amount on the oxidation of benzyl alcohol.

conversion was obtained. Therefore, 1 mL H_2O_2 30% was chosen as the optimized amount of oxidant. In the absence of the oxidant, only 12% of benzaldehyde was obtained after 4.5 h (table 3, entry 5). This result showed that the presence of the oxidant is essential in this oxidation reaction.

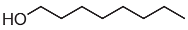
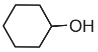
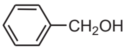
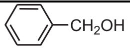
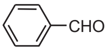
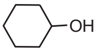
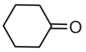
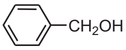
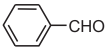
The effect of reaction temperature on the oxidation of benzyl alcohol with H_2O_2 catalyzed by **1**-POM(Zn) was also investigated. The results showed that only small

Table 3. Selective oxidation of alcohols using H_2O_2 catalyzed by **1**-POM(Zn).[a]

Entry	Substrate	Product	Time (h)	Yield (%)[b]
1			4.5	100
2			3	98
3			4	98
4			4	95
5			3.5	97
6			4	93
7			5	87
8			5.5	76
9			6	66
10			7	61
11			7	82
12			7	34
13			5.5	26
14			4	95
15			6	–

(*Continued*)

Table 3. (*Continued*).

Entry	Substrate	Product	Time (h)	Yield (%)[b]
16	  	  (2)	4.5	(1) 13 (2) 85
17	  (1)	  (2)	4.5	(1) 0 (2) 91

[a] Reaction conditions: alcohol (1 mmol), H_2O_2 (1 mL), **1**-POM(Zn) (0.05 mmol), CH_3CN (3 mL).
[b] GC yield.

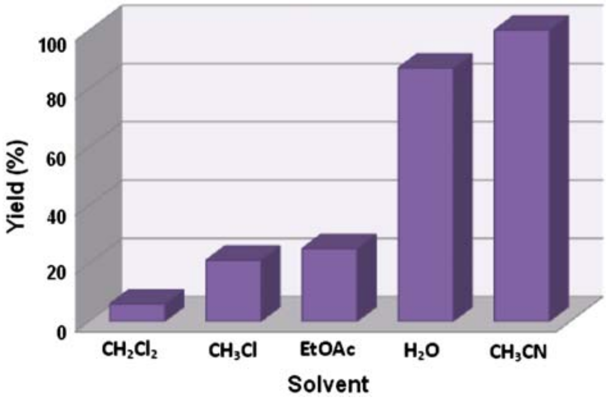


Figure 4. The effect of solvent on the oxidation of benzyl alcohol.

amounts of benzaldehyde was produced (<5%) at room temperature, while under reflux, both conversion and selectivity were increased. Acetonitrile, dichloromethane, ethyl acetate, chloroform, and water were tested as solvents in the same reaction. Acetonitrile was chosen as the best reaction solvent, because a higher catalytic activity was observed. The higher catalytic activity in acetonitrile is attributed to the polarity and solubility of the substrate in the solvent (figure 4).

Oxidations of various alcohols including linear, cyclic, and aromatic ones bearing different functional groups were performed under optimized reaction conditions (table 3). The results showed electron-rich alcohols are more reactive than electron-poor ones. Compared to benzylic alcohols, aliphatic alcohols showed relatively low activity toward oxidation. This is due to the higher stability of carbocation for benzylic alcohols in comparison with linear ones. In order to show the chemoselectivity of this heterogeneous catalytic system, an equimolar mixture of primary and benzylic alcohols was subjected to oxidation. For example, in the oxidation of 1-octanol and benzyl alcohol, the amount of 1-octanal was less than 13%, while benzyl alcohol was converted to benzaldehyde in 85% yield. On the

Table 4. Comparison of results for the oxidation of benzyl alcohol catalyzed by **1**-POM(Zn) with reported catalytic systems.

Entry	Oxidant	Catalyst	Time (h)	Yield (%)	Ref.
1	H_2O_2	**1**-POM(Zn)	4.5	100	This work
2	H_2O_2	$[bmim]_5[PW_{11}ZnO_{39}]\cdot3H_2O$	1.25	100	[44]
3	H_2O_2	$[(C_{18}H_{37})_2(CH_3)_2N]_7[PW_{11}O_{39}]$	7	56	[45]
4	O_2	$H_3PW_{12}O_{40}/ZrO_2$	4	81	[32]
5	H_2O_2	$[VO(L)_2]$–Oxone–*n*-Bu_4NBr	0.5	41	[46]
6	H_2O_2	PS-IL-[*a*-$PW_{12}O_{40}$]	12	100	[47]
7	C_6H_5IO	[Mn(III)(salen)Cl]	2	89	[48]

Table 5. The results of **1**-POM(Zn) recovery in the oxidation of benzyl alcohol.[a]

Run	Conversion (%)[b] after 4.5 h	Amount of Zn leached (%)[c]
1	100	0.6
2	99	0
3	97	0
4	97	0
5	95	0

[a] Reaction conditions: Benzyl alcohol (1 mmol), H_2O_2 (1 mL), **1**-POM(Zn) (0.05 mmol), CH_3CN (3 mL).
[b] GC yield.
[c] Determined by atomic absorption spectroscopy.

other hand, in the oxidation of a mixture of cyclohexanol and benzyl alcohol, only benzaldehyde was produced in 91% yield (table 3, entries 16 and 17). This clearly reveals that this method can be applied for the chemoselective oxidation of benzylic alcohols in the presence of primary and secondary alcohols.

To show the efficiency of this catalyst, oxidation of benzyl alcohol was compared with those reported in the literature (table 4) [32, 44–48]. The results show that our reported method is superior in terms of reaction time and/or product yield or catalyst reusability.

3.3. *Catalyst recovery and reuse*

The reusability of this heterogeneous hybrid catalyst, **1**-POM(Zn), was examined using benzyl alcohol as a model substrate. For each of the repeated reactions, after 4.5 h, the catalyst was filtered, washed with *n*-hexane, and dried at room temperature. As shown in table 5, the catalyst was reused seven times without a detectable catalyst leaching or a significant loss of its activity. The FT IR and solid UV–vis spectra showed no significant structural changes for catalyst **1**-POM(Zn) after five consecutive runs (Supplementary material).

4. Conclusion

The organic–inorganic hybrid catalysts **1**-POM(M) were prepared by the reaction of tris[2-(dimethylammonium)ethyl]-1,3,5-benzenetricarboxylate and transition metal-substituted POMs, $\{[PW_{11}MO_{39}]^{4-}$ [M = Cr(III), Fe(III)], $[PW_{11}MO_{39}]^{5-}$ [M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)], $[PW_{11}VO_{40}]^{4-}\}$, and characterized by elemental analyses, UV–vis, FT IR spectroscopic techniques, XRD, SEM, and TG–DTG analyses. These hybrid catalysts were applied for selective oxidation of alcohols to aldehydes and ketones with hydrogen peroxide. The results indicated that **1**-POM(Zn) is a green, selective, and efficient catalyst for alcohol oxidation. The hybrid catalyst **1**-POM(Zn) is a heterogeneous catalyst and can be easily separated and reused several times.

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