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Solvent-Free Selective Oxidation of Benzyl Alcohol to Benzaldehyde Catalyzed by Zinc Mono-Substituted Phosphotungstic Acid Quaternary Ammonium Salt

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Abstract: A series of Zn-substituted Keggin phosphotungstic acid quaternary ammonium salt catalysts were prepared, and characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD). Their catalytic activities were evaluated by the oxidation of benzyl alcohol to benzaldehyde with H_2O_2 under solvent-free conditions. The effects of reaction parameters on the oxidation of benzyl alcohol were also investigated in detail. All the catalysts show good catalytic activity with fast reaction rate, eco-friendly and excellent selectivity for the desired products. In the absence of any solvent, the conversion of benzyl alcohol and the selectivity of benzaldehyde were found to be as high as 95.6% and 96.4% under optimum conditions in just 30 min. And a possible reaction mechanism of the oxidation of benzyl alcohol was deduced.

Key words: transition metal Zn; phosphotungstic acid quaternary ammonium salt; benzyl alcohol; solvent-free oxidation
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Catalytic oxidation of benzyl alcohol to benzaldehyde has become an important synthetic reaction with numerous applications in fine chemistry. Traditionally, the oxidation of benzyl alcohol was carried out using stoichiometric amounts of inorganic oxidants (e.g. sodium dichromate, sodium hypochlorite, manganese dioxide, potassium permanganate, etc.), these oxidants suffer from several drawbacks such as relatively expensive and commonly hazardous or toxic accompanying the generation of high amounts of heavy-metal waste[1]. Therefore, the exploiting of more active, efficient, green and environmentally catalysts to activate H_2O_2 and O_2 for the oxidation of benzyl alcohol to benzaldehyde has been received considerable attention in both academia and industry. In this regard, studies on the oxidation of benzyl alcohol using H_2O_2 and O_2 have been investigated using different type of catalysts and a variety of operating conditions. The reaction was studied using several types of metal-based catalysts, such as Ru, Pd, and Au[2-3], as well as the transition metal of hydrotalcite-like compounds[4], the modified zeolite molecular sieve[5], other transition metal compounds[6] and Schiff base complex[7-8]. However, catalytic reactions have been carried out at higher temperature, using organic solvent or relatively expensive transition metals (Ru, Pd, and Au). In addition, a series of Cu based catalysts have been developed for the oxidation of benzyl alcohol to benzaldehyde[9], but the poisonous hydrocarbon was used as the solvent and used copper halide as the catalyst, which also cause environmental pollution.

Heteropolyacids (HPAs) are metal-oxo anionic clusters whose chemical properties can be controlled by transition metal substitution and the countercation used[10], which have been found wide applications in many fields, such as catalysis, medicine, magnetic properties, materials, surface chemistry and photochromism and electrochromism[11]. Among HPAs, transition metal mono-substituted Keggin heteropoly anion α-$[XW_{11}MO_{39}]^{(n-m)-}$($X$ = P, Si), in which a transition metal cation M^{m+} is coordinated to the binding sites of lacunary heteropoly anions α-$[XW_{11}O_{39}]^{n-}$, have

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generated great interest as oxidative catalysts[12]. Their thermal and chemical stability as well as redox and acidic properties could be controlled at the atomic/molecular level by changing addenda atoms without affecting the Keggin primary structure[13]. Furthermore, HPAs is commonly combined with different cationic species, allowing their solubilisation in different media, for example films and supports[14-15]. In this context, many efforts have been devoted to study the oxidation of benzyl alcohol to benzaldehyde in the presence of transition metal mono-substituted Keggin HPAs catalysts. For example, Nadealian and co-workers reported that $[\text{bmim}]_x[\text{PW}_{11}M\text{O}_{39}]$ (bmim = 1-n-butyl-3-methylimidazolium and $M = \text{V}^{5+}$, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) exhibits high catalytic activity for the oxidation of benzyl alcohol into benzaldehyde using acetonitrile as solvent[16]. Wang *et al.* studied the oxidation of benzyl alcohol over a series of transition metal (M = Zn, Cu, Ni, Co, Fe, Mn, Cr, V) mono-substituted silicotungstic acid salts using hydrogen peroxide as oxidant[17]. Also, $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ functionalized by cationic surfactants cations, and $[\text{PMo}_{11}M]^{5-}$(M = Co, Mn, Ni) have been reported to be efficient catalysts for the oxidation of benzyl alcohol[18-19]. In the case of transition metal mono-substituted Keggin HPAs, most of the works have been conducted on vanadium, cobalt, nickel and manganese mono-substituted Keggin HPAs. In addition, catalytic oxidation requires longer reaction time (more than 5 hours) or the use of organic solvents.

Although a number of methods have been developed, the development of cost-effective and eco-friendly procedures avoiding the use of toxic solvents and oxidants still attracts substantial interest. To date, Studies on Zinc mono-substituted phosphotungstic acid quaternary ammonium salt under mild reaction conditions are not available. In this work, we designed and synthesized a series of Zn mono-substituted Keggin phosphotungstic acid quaternary ammonium salt $\text{Q}_4\text{H}_x\text{PW}_{11}\text{ZnO}_{39}$[$\text{Q} = (\text{C}_4\text{H}_9)_4\text{N}$, $\text{C}_7\text{H}_7(\text{CH}_3)_3\text{N}$, $\text{C}_{12}\text{H}_{25}(\text{CH}_3)_3\text{N}$, $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}$, $\text{C}_{18}\text{H}_{37}(\text{CH}_3)_3\text{N}$] catalysts for the oxidation of benzyl alcohol with H_2O_2. These catalysts show the feature of the fast reaction rate, high conversion and selectivity under a solvent-free condition. The conversion of benzyl alcohol and the selectivity of benzaldehyde were found to be up to 95.6% and 96.4% (just 30 min). Finally, a possible mechanism of the oxidation of benzyl alcohol was proposed.

1 Experimental section

1.1 Catalyst preparation

The following procedure for the preparation of Zn-substituted Keggin phosphotungstic acid tetrabutylammonium salt $[(\text{C}_{16}\text{H}_{36}\text{N})_4\text{H}_x\text{PW}_{11}\text{ZnO}_{39}]$, 2.275 mmol of $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ was firstly dissolved in 20 mL of water. Then 25 mmol solid of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added to this solution, after the solid material dissolved, 3 mmol of $\text{Zn(NO}_3)_2$ dissolved in 30 mL of water was added, the pH of the solution was adjusted to 4.8 using a nitric acid solution[20-21]. The solution was heated at 85 ℃ and 11.25 mmol of tetrabutylammonium bromide dissolved in 5 mL of water was added, the mixture was stirred for 3 h at 85 ℃. The resulting pure white precipitate was filtered off and recrystallized from acetonitrile, dried at 80 ℃ for 12 h and designated as $\text{C}_{16}\text{H}_{36}\text{NPW}_{11}\text{Zn}$.

Other Zn-substituted phosphotungstic acid quaternary ammonium salt were also synthesized according to a similar method by taking the corresponding quaternary ammonium salt (dodecyl trimethyl quaternary ammonium salt, cetyl trimethyl quaternary ammonium salt, and octadecyl trimethyl quaternary ammonium salt). As obtained catalysts were very poorly soluble in any solvent, no recrystallization was carried out. The obtained catalysts were designated as $\text{C}_{10}\text{H}_{16}\text{N}_4\text{PW}_{11}\text{Zn}$, $\text{C}_{15}\text{H}_{34}\text{NPW}_{11}\text{Zn}$, $\text{C}_{16}\text{H}_{36}\text{NPW}_{11}\text{Zn}$, $\text{C}_{19}\text{H}_{42}\text{NPW}_{11}\text{Zn}$, and $\text{C}_{21}\text{H}_{46}\text{NPW}_{11}\text{Zn}$, respectively.

1.2 Characterizations of the samples

The synthesized compounds were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The Fourier transform infrared spectroscopy studies were done on American Nicolet Nexus 670 Fourier transform infrared spectrometer in KBr matrix in the range of 4 000 ~ 600 cm^{-1}. The powder XRD pattern was obtained by using a Rigaku D/

Max - 2400 X-ray diffractometer with Cu Kα radiation (1.54 Å) at 40 kV and 150 mA in the range of $2\theta = 5° \sim 40°$ with a step size of 0.02°.

1.3 Catalytic oxidation of benzyl alcohol

A 100 mL two-necked round bottom flask, fitted with a reflux condenser and magnetic stirrer was used as a reactor. A typical procedure for the oxidation of benzyl alcohol was carried out as follows: a measured amount of $Q_4H_xPW_{11}ZnO_{39}$ was added into a two-necked flask containing benzyl alcohol. When the temperature was raised up to desired temperature, a measured amount of 30% H_2O_2 was added to the reaction mixture. After reaction, the mixture was cooled to room temperature. The product was extracted with acetic ether, and the organic phase was analyzed by GC7890II with a flame ionization detector, using a SE-54 capillary column (0.32 mm × 0.5 μm × 30 m) and N_2 as carrier gas (injector temp. 150 ℃, detector temp. 280 ℃, Column temp. 280 ℃, N_2 pressure: 0.1 MPa). The conversion and selectivity of the products were calculated based on the component contents and were analyzed by an internal standard method.

2 Results and discussion

2.1 Catalyst characterization

The FTIR spectra give information regarding the incorporation of Zn into the lacuna of the phosphotungstic acid. The FTIR spectra of $C_{10}H_{16}N_4PW_{11}Zn$, $C_{15}H_{34}NPW_{11}Zn$, $C_{16}H_{36}NPW_{11}Zn$, $C_{19}H_{42}NPW_{11}Zn$, and $C_{21}H_{46}NPW_{11}Zn$ are shown in Fig. 1. As can be predicted from Fig. 1, the spectra of these prepared heteropoly compounds show the characteristic bands at 1 100 ~ 700 cm^{-1} region, indicating that the synthesized heteropoly compounds have the structure of Keggin anion. The intense and broad bands at 3 460 cm^{-1} is attributed to the hydroxyl groups and water molecules. The characteristic vibrations attributable to the quaternary ammonium cations at 2 960 cm^{-1} (ν_{as} CH_2), 2 871 cm^{-1} (ν_s CH_2), and 1 483 cm^{-1} (δ CH_2), and to $[PW_{11}Zn]^{5-}$ anion at 1 100 ~ 1 050 cm^{-1} (ν_{as} P-Oa), 960 cm^{-1} (ν_{as} W=Od), 892 cm^{-1} (ν_{as} W-Ob-W), 821 cm^{-1} (ν_{as} W-Oc-W), and 740 cm^{-1} (ν_{as} W-O-Zn) appear in the FTIR spectra of $C_{10}H_{16}N_4PW_{11}Zn$, $C_{15}H_{34}NPW_{11}Zn$, $C_{16}H_{36}NPW_{11}Zn$, $C_{19}H_{42}NPW_{11}Zn$, and $C_{21}H_{46}NPW_{11}Zn$, respectively. However, The P-Oa band at 1 080 cm^{-1} for $[PW_{12}O_{40}]^{3-}$ actually split into two bands at 1 088 cm^{-1} and 1 055 cm^{-1} for $[PW_{11}Zn]^{5-}$ due to the variation of the symmetry of PO_4 tetrahedron[22]. The value of the difference of the split bands ($\Delta\nu$) is around 33 cm^{-1}, the $\Delta\nu$ value observed is in good agreement with that reported previously[23]. According to Varadwaj *et al.* description[24], the $\Delta\nu$ values provide an indirect measure of the interaction between the metal atom and available oxygen of the central PO_4 tetrahedron, the higher will be the interaction for lower $\Delta\nu$ value. Therefore, the FTIR spectra clearly show that Zn atoms have been successfully incorporated into the Keggin framework. The P-Oa bond cleavage and the appearance of W-O-Zn bridge bond vibration bands are the principal methods to judge the incorporation of metal atoms into HPAs primary structure[25].

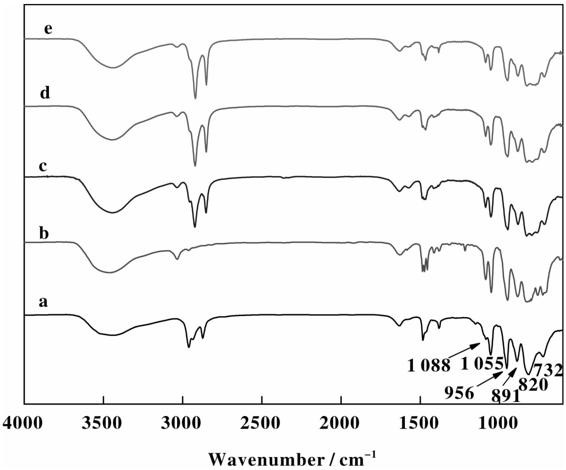


Fig. 1 FTIR spectra of Zn-substituted phosphotungstic acid quaternary ammonium salt

a - $C_{16}H_{36}NPW_{11}Zn$; b - $C_{10}H_{16}NPW_{11}Zn$; c - $C_{15}H_{34}NPW_{11}Zn$; d - $C_{19}H_{42}NPW_{11}Zn$; e - $C_{21}H_{46}NPW_{11}Zn$

The powder X-ray diffraction (XRD) patterns are displayed in Fig. 2. According to the existing literature[22], the neat Keggin phosphotungstic acid exhibits a set of well sharp diffraction peaks featured for the secondary crystal structure of Keggin HPAs in the range of 7° ~ 12°, 16° ~ 22°, 25° ~ 30°, 33° ~ 38°,

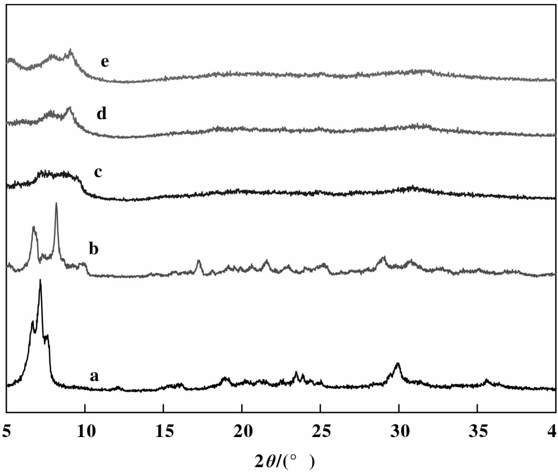


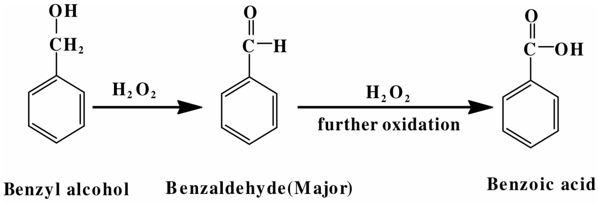
Fig. 2 The XRD patterns of Zn-substituted phosphotungstic acid quaternary ammonium salt

a - $C_{16}H_{36}NPW_{11}Zn$; b - $C_{10}H_{16}NPW_{11}Zn$; c - $C_{15}H_{34}NPW_{11}Zn$; d - $C_{19}H_{42}NPW_{11}Zn$; e - $C_{21}H_{46}NPW_{11}Zn$

in contrast, the XRD patterns of $Q_4H_xPW_{11}ZnO_{39}$ particles show that the well sharp diffraction peaks disappeared in diffraction profile compared to that of the neat Keggin phosphotungstic acid, implying that the $Q_4H_xPW_{11}ZnO_{39}$ particles have the same no-crystal feature. Furthermore, $C_{16}H_{36}NPW_{11}Zn$ and $C_{10}H_{16}NPW_{11}Zn$ show stronger characteristic diffraction peaks in the range of 7° ~ 12°, 16° ~ 22°, 25° ~ 30°, 33° ~ 38°, assigning to the Keggin HPAs anion characteristic diffraction peaks. However, with the increase of the quaternary ammonium cation carbon-chain length, the peak intensity of heteropoly compounds characteristic diffraction obviously decreased in the range of 5° ~ 40°. All samples show the only broad Bragg reflection in the small angle range of 5° ~ 10°, indicating that there are the existence of very small gaps between quaternary ammonium cations and $[PW_{11}Zn]^{5-}$ anions[26]. The small gaps may accelerate the permeation of the polar alcohol substrates into the bulk of the Zn-substituted Keggin phosphotungstic acid quaternary ammonium salt, and the phenomenon is similar to the viewpoint of "pseudo-liquid behavior" for the bulk-type catalysis of a HPAs catalyst[27]. This fact was also reported by Leng *et al.* [28].

2.2 Catalytic oxidation of benzyl alcohol

The oxidation of benzyl alcohol was studied under solvent-free conditions in the presence of Zn-substituted Keggin phosphotungstic acid quaternary ammonium salt $Q_4H_xPW_{11}ZnO_{39}$. Generally, benzyl alcohol is firstly oxidized to benzaldehyde, and benzaldehyde is further oxidized to benzoic acid (scheme 1). However, in the present reaction conditions, the oxidation products of benzyl alcohol were analyzed by the gas chromatograph, the major oxidation product obtained was benzaldehyde, and a small amount of benzoic acid was only detected, indicating the prepared $Q_4H_x[PW_{11}ZnO_{39}]$ catalysts have an excellent catalytic activity on the oxidation of benzyl alcohol to benzaldehyde.



Scheme1 Oxidation of benzyl alcohol with H_2O_2

As shown in Table 1, $H_3PW_{12}O_{40}$ catalyst shows low activity, the conversion of benzyl alcohol and the selectivity of benzaldehyde were measured to be only 26.9% and 77.1% (Table 1, entry 2), but in the presence of $Na_5PW_{11}ZnO_{39}$, the conversion of benzyl alcohol and the selectivity of benzaldehyde were increased up to 34.3% and 99.7% (Table 1, entry 3), implying that the Zn species have essential roles in the oxidation reaction. The observed phenomenon is in good agreement with previous work reported by Zahra Nadealian and his co-workers[17]. The catalytic activity of various Zn-substituted Keggin phosphotungstic acid quaternary ammonium salt catalysts was also checked in oxidation of benzyl alcohol with H_2O_2. Although tetrabutylammonium bromide itself was inactive in the oxidation (Table 1, entry 1), the conversion of benzyl alcohol and the selectivity of benzaldehyde were found to be as high as 95.6% and 96.4% using $C_{16}H_{36}NPW_{11}Zn$ as catalyst. Among $Q_4H_xPW_{11}ZnO_{39}$ catalysts containing various quaternary ammonium cations, $C_{16}H_{36}NPW_{11}Zn$ catalyst shows the highest catalytic performance in oxidation of benzyl alcohol (Table 1, entry 4), and $C_{10}H_{16}NPW_{11}Zn$ catalyst shows lowest catalytic performance (Table 1, entry 5), this should be attributed to the fact that $C_{10}H_{16}NPW_{11}Zn$ catalyst was insoluble and others completely dissolved during the reaction. The results also indicate that there are the existence of a synergistic effect between quaternary ammonium cations and $[PW_{11}Zn]^{5-}$, which is responsible for the oxidation of benzyl alcohol.

Table 1 Oxidation of benzyl alcohol with H_2O_2

Entry	Catalyst	Reaction time/min	Conversion of benzyl alcohol/%	Selectivity of benzaldehyde/%	Selectivity of benzoic acid/%
1	tetrabutylammonium bromide	30	0	0	0
2	$H_3PW_{12}O_{40}$	30	26.9	77.1	22.9
3	$Na_5PW_{11}ZnO_{39}$	30	34.3	99.7	0.3
4	$C_{16}H_{36}NPW_{11}Zn$	30	95.6	96.4	3.6
5	$C_{10}H_{16}NPW_{11}Zn$	30	67.7	94.2	5.8
6	$C_{15}H_{34}NPW_{11}Zn$	30	93.1	95.8	4.2
7	$C_{19}H_{42}NPW_{11}Zn$	30	91.6	94.4	5.6
8	$C_{21}H_{46}NPW_{11}Zn$	30	92.2	95.3	4.7

Reaction conditions: 0.1 mol benzyl alcohol, 0.105 mol H_2O_2, reaction temperature 90°C, reaction time 30 min, amount of catalyst 0.2 mmol.

2.3 Optimization of reaction conditions

2.3.1 Effect of reaction temperature The effect of reaction temperature on the oxidation of benzyl alcohol is shown in Fig. 3. The reaction was carried out in the temperature region 70 ~ 110 ℃ using $C_{16}H_{36}NPW_{11}Zn$ as the catalyst with the other parameters fixed. It can be seen that the maximum conversion of benzyl alcohol and the maximum selectivity of benzaldehyde were measured to be 95.6% and 96.4% at 90 ℃. On the other hand, the results show that the conversion of benzyl alcohol increased with increasing temperature from 70 to 110 ℃. Especially, on increasing the temperature from 70 to 80 ℃, a drastic increase in the conversion of benzyl alcohol was observed, but there was no appreciable increase for the benzyl alcohol conversion at elevated reaction temperature (> 90 ℃). However, the selectivity of benzaldehyde decreased with an increase of reaction temperature, which is attributed to the fact that the desired product benzaldehyde is further oxidized to benzoic acid at elevated temperature. Thus, 90 ℃ was an appropriate reaction temperature for the oxidation of benzyl alcohol to benzaldehyde in the following experiments.

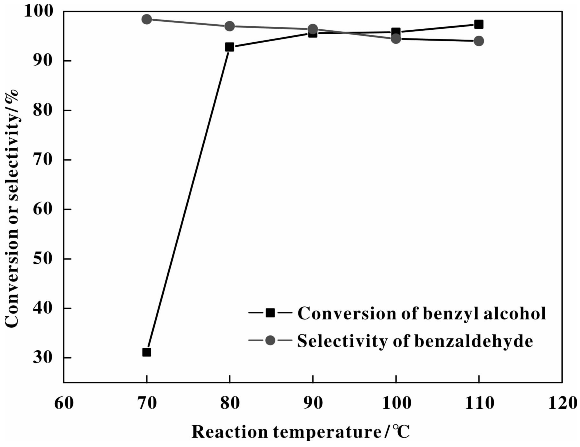


Fig. 3 Effect of reaction temperature on the oxidation reaction
Reaction conditions: Catalyst, $C_{16}H_{36}NPW_{11}Zn$; Reaction time, 30 min; Amount of catalyst, 0.2 mmol; Benzyl alcohol, 0.1 mol; H_2O_2, 0.105 mol

2.3.2 Effect of reaction time Fig. 4 shows the effect of reaction time on the conversion of benzyl alcohol and the selectivity of benzaldehyde. It can be seen that an increasing trend was observed for the conversion of benzyl alcohol with prolonging the reaction time. Initially, the conversion of benzyl alcohol dramatically increased with prolonging the reaction time. This is due to the fact that more time is required for the formation of the reactive intermediate which is finally converted into the products[29]. When the reaction was allowed to continue after 30 min, only a slight change in the conversion was observed. This is because that the decomposition of H_2O_2 increases with prolonging the reaction time, the decomposition of H_2O_2 is a competitive reaction for the oxidation of benzyl alcohol. Moreover, the over oxidation of benzaldehyde to benzoic acid occur with prolonging the reaction time. It was found that the selectivity of benzaldehyde always decreased with an increase in reaction time. Hence, further optimization of the conditions was carried out with 30 min.

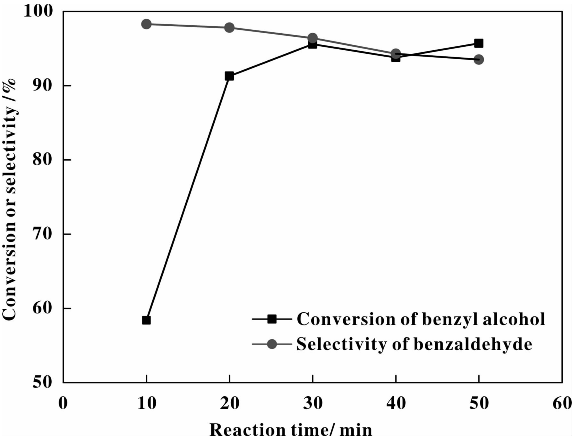


Fig. 4 Effect of reaction time on the oxidation reaction
Reaction conditions: Catalyst, $C_{16}H_{36}NPW_{11}Zn$;
Reaction temperature, 90°C; Amount of catalyst,
0.2 mmol; Benzyl alcohol, 0.1 mol; H_2O_2, 0.105 mol

2.3.3 Effect of amount of the catalyst The amount of catalyst has a significant effect on the oxidation of benzyl alcohol. The effects of the catalyst amount were investigated with $C_{16}H_{36}NPW_{11}Zn$ catalyst (Fig. 5). As seen in the results, with an increase in the catalyst amount from 0.10 mmol to 0.30 mmol, the conversion of benzyl alcohol increased from 75.0% to 96.5%, while the selectivity of benzaldehyde remained almost constant (>95%). When the catalyst amount was 0.10 mmol, a conversion of benzyl alcohol 75.0% was obtained after 30 min. This is attributed to the fact that the low amount of catalyst is unable to effectively catalyze the oxidation of benzyl alcohol, and the number of active sites (i. e. amount of Zn species) increases with increasing in the amount of catalysts. The maximum conversion of benzyl alcohol was observed with 0.2 mmol of catalyst, but there was no remarkable difference in the progress of reaction when 0.25 mmol of catalyst was employed. However, the catalyst amount had a negligible influence on the selectivity of benzaldehyde. Therefore, 0.2 mmol of the catalyst was selected for the optimum conversion and selectivity.

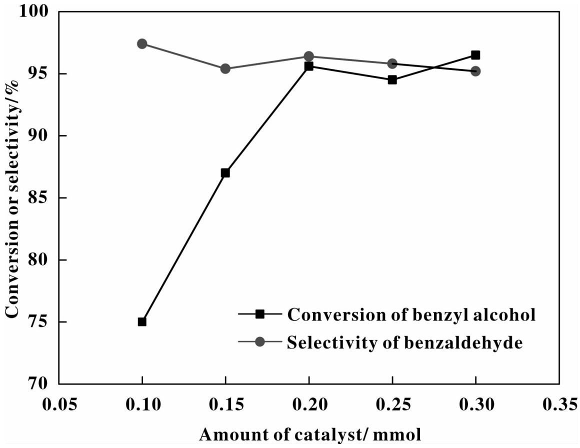


Fig. 5 Effect of catalyst amount on the oxidation reaction
Reaction conditions: Catalyst, $C_{16}H_{36}NPW_{11}Zn$;
Reaction temperature, 90°C; Reaction time, 30 min;
Benzyl alcohol, 0.1 mol; H_2O_2, 0.105 mol

2.3.4 Effect of amount of H_2O_2 The amount of H_2O_2 used in this system is another important factor influencing the oxidation of benzyl alcohol. It is observed from Fig. 6 that there was a significant change in the

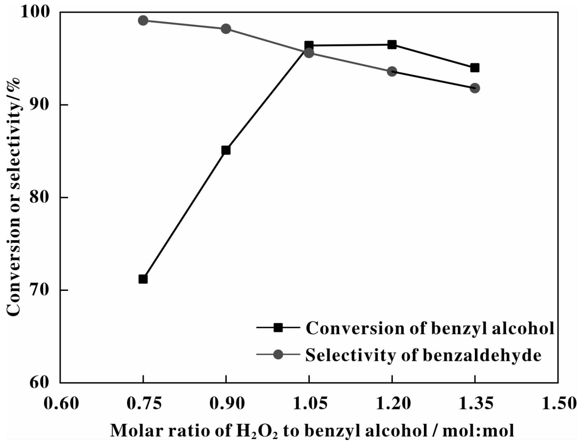


Fig. 6 Effect of amount of H_2O_2 on the oxidation reaction
Reaction conditions: Catalyst, $C_{16}H_{36}NPW_{11}Zn$;
Reaction temperature, 90 ℃; Benzyl alcohol, 0.1 mol;
Reaction time, 30 min; Amount of catalyst, 0.2 mmol

conversion of benzyl alcohol with an increase in the mole ratio of H_2O_2 : benzyl alcohol from 0.75 : 1 to 1.05 : 1. At the same time, the selectivity of benzaldehyde always decreased with an increase of the mole ratio of H_2O_2 : benzyl alcohol. The decrease of the selectivity of benzaldehyde should be attributed to the increase of amount of H_2O_2 which induce further oxidation of benzaldehyde into benzoic acid. Therefore, the optimum molar ratio of H_2O_2 : benzyl alcohol was 1.05 in the conducted reaction conditions.

The optimum conditions for the oxidation of benzyl alcoholusing $C_{16}H_{36}NPW_{11}Zn$ as catalyst are: reaction temperature 90 ℃, reaction time 30min, amount of the catalyst 0.20 mmol, the molar ratio of H_2O_2 : benzyl alcohol was 1.05. Under optimum conditions, the conversion of benzyl alcohol and the selectivity of benzaldehyde were measured to be as high as 95.6% and 96.4%.

2.4 Probable reaction mechanism

According to previous literatures[17, 30-31], when the oxidation reaction is carried out with transition metal substituted HPAs catalyst, the transition metals commonly act as catalytic active centers, and the transition metals react with H_2O_2 to produce active species ($M\text{-}O_2$) which is an active intermediate for the oxidation of substrate. Based on these views, a possible mechanism involving the catalytic intermediate species was proposed (Fig. 7). At the beginning of the reaction, the $Q_4H_x[PW_{11}ZnO_{39}]$ (species 1) catalyst gets attached with H_2O_2 species and forms the peroxo metal species 2 which then attacks benzyl alcohol. The metal peroxo metal intermediate (species 2) reversibly binds benzyl alcohol to form a transient species 3. The species 3 is unstable, so a molecule of water would be lost from the transient species 3, and the other intermediate species 4 is form. Finally, the intermediate species 4 dissociate to form products with a loss of water molecule. Thus, it is believed that the activated peroxo metal species 2 may be responsible for the oxidation of benzyl alcohol. A similar mechanism analysis can be seen in the previously reported paper[32].

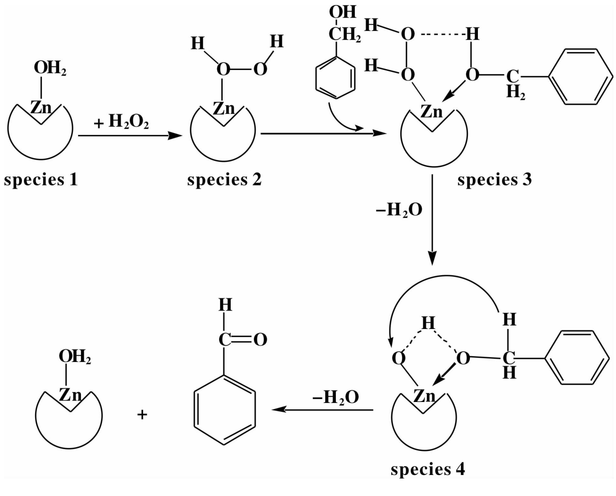


Fig. 7 Possible mechanism for oxidation of benzyl alcohol to benzaldehyde with H_2O_2

3 Conclusion

In summary, we have developed a series of Zn-substituted Keggin phosphotungstic acid quaternary ammonium salt $Q_4H_xPW_{11}ZnO_{39}$ catalysts. The compounds were characterized by FTIR and XRD. FTIR results reveal that Zn atoms have been successfully incorporated into the Keggin framework, and indicate that $Q_4H_xPW_{11}ZnO_{39}$ retained its parent Keggin structure. XRD results show that the $Q_4H_xPW_{11}ZnO_{39}$ particles have the same no-crystal feature. Moreover, the XRD pattern of synthesized compounds indicate the existence of very small gaps between quaternary ammonium cations and $[PW_{11}Zn]^{5-}$ anions, which may accelerate the permeation of benzyl alcohol into the bulk of the Zn-substituted Keggin phosphotungstic acid quaternary ammonium salt. In addition, these catalysts were proven to be an efficient catalyst for the oxidation of benzyl alcohol to benzaldehyde with H_2O_2 under solvent-free conditions. Therefore, the as-synthesized Zn-substituted phosphotungstic acid quaternary ammonium salt catalysts have great potential application for the catalytic oxidation of benzyl alcohol to benzaldehyde. Compared with conventional catalytic systems, the present catalytic system offers significant improvements with regard to catalytic efficiency, cost efficiency, and green aspects avoiding toxic oxidants and solvents. Under optimum conditions, the conversion of benzyl alcohol and the selectivity of benzaldehyde were measured to be as high as 95.6% and 96.4%.

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Zn 取代的磷钨酸季铵盐无溶剂氧化苯甲醇合成苯甲醛

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摘要：合成了一系列过渡金属 Zn 取代的 Keggin 型磷钨杂多酸的季铵盐，采用傅里叶变换红外光谱（FTIR）、X 射线衍射（XRD）等方法表征了杂多化合物的结构. 并将其用于苯甲醇无溶剂氧化合成苯甲醛的反应，考察了催化剂种类、反应条件对苯甲醇氧化的影响. 实验结果表明，在无任何溶剂的情况下，Zn 取代的 Keggin 型磷钨四丁基铵盐具有最佳的催化活性，反应时间仅为 30 min，苯甲醇的转化率可以达到 95.6%，苯甲醛的选择性达到了 96.4%. 在对杂多酸季铵盐结构的研究基础上，对可能的反应机理进行了初步探讨.

关键词：过渡金属 Zn；磷钨酸季铵盐；苯甲醇；无溶剂氧化