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Article

Selective oxidation of benzyl alcohol catalyzed by $(\text{TEAH})_n\text{H}_{3-n}\text{PW}_{12}\text{O}_{40}$ and its reaction mechanism

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ABSTRACT

Several triethylamine (TEA) salts of phosphotungstic acid were synthesized by an acid-base reaction using a Keggin-type phosphotungstic acid and TEA, and used to catalyze the oxidation of benzyl alcohol to benzaldehyde in water with 30% aqueous hydrogen peroxide as oxidant. $(\text{TEAH})_n\text{H}_{3-n}\text{PW}_{12}\text{O}_{40}$ ($n = 1, 2, 3$) were excellent catalysts for the reaction and could be isolated and recycled. With $(\text{TEAH})_2\text{H}_2\text{PW}_{12}\text{O}_{40}$, the conversion of benzyl alcohol and selectivity to benzaldehyde were as high as 99.6% and 100%, respectively, under optimized reaction conditions. The catalysts and their transformation and distribution during the reaction were investigated by IR, ^{31}P NMR and analysis of the reaction system, and the reaction mechanism was deduced. In this water-oil biphasic reaction, $(\text{PW}_{12}\text{O}_{40})^{3-}$ was first oxidized and degraded into small $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ and free tungsten species that were soluble in the aqueous phase upon reaction with H_2O_2 . Then $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$, as the actual oxidant, oxidized benzyl alcohol soluble in the aqueous phase to benzaldehyde, and was converted into a SAR (species after reaction) after losing its active oxygen. The catalytic cycle was completed by the polymerization of the SAR with the free tungsten species back to larger catalyst precursor $(\text{PW}_{12}\text{O}_{40})^{3-}$, which was soluble in the oil phase.

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1. Introduction

Benzaldehyde is an important chemical intermediate and raw material widely used in the manufacture of perfumes, agricultural chemicals, spices and other fine chemicals. In view of the many drawbacks of traditional synthesis methods, such as toluene chlorination hydrolysis and toluene oxidation [1], the preparation of benzaldehyde by the oxidation of benzyl alcohol has received much attention [2]. From the viewpoint of green chemistry, the use of low concentration hydrogen peroxide, which is cheap, mild and clean for the environment, as the oxidant for this reaction undoubtedly makes this a very competitive way. In the oxidation involving H_2O_2 , polyoxometalate

(POM) as an efficient and environment-friendly catalyst is often employed to construct the POM/ H_2O_2 oxidation system, which has been applied in the epoxidation of olefins [3,4], oxidation of alcohols [4–6], and oxidation of aromatics [7,8]. For the selective oxidation of benzyl alcohol, the POM/ H_2O_2 system also exhibited excellent catalytic performance. Because water-soluble POMs cannot be recovered after the reaction, recycle of the catalyst was performed by isolating and reusing the aqueous phase in this water-oil biphasic reaction [9,10]. For the easy recovery of the catalyst, POMs have been designed as supported catalysts [11,12] or reaction-controlled phase transfer catalysts [13,14], and an organic solvent is used usually in the latter system. Recently, studies on ionic liquid-like POM catalysts

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showed that some of them [15] and those supported on silica [16], mesoporous molecular sieve [17,18] and organic polymer [19] also gave high catalytic activity and could be recycled in the oxidation of benzyl alcohol. But in general, the preparation of these catalysts is complex and their cost is high.

Studies on the oxidation mechanism in the POM/ H_2O_2 system were mostly focused on the epoxidation of olefins, and start from the Venturello-Ishii system of POM/ H_2O_2 /phase transfer agent/organic solvent [4,20,21]. Many studies [4,20–25] have proved that small peroxo active species PX_nO_x (such as $(\text{PO}_4(\text{XO}(\text{O}_2)_2)_4)^{3-}$, $\text{X} = \text{W}, \text{Mo}$) were first formed as the actual oxidative reagent from the reaction of the POM precursor (such as PW_{12} or PMo_{12}) with hydrogen peroxide. After the olefin was oxidized, the catalyst returned to the precursor state and the catalytic cycle was completed. However, studies on the mechanism of alcohol oxidation are few and rough [10,14]. Zhang et al. [5] reported that $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ was also active for the oxidation of alcohol and was the sole small PW species detected in the reaction. They indicated that the reaction was mainly carried out in the organic phase and a transform-and-retransform process occurred between PW_{12} and $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$. However, for the oxidation of benzyl alcohol in the absence of a phase transfer catalyst with a long chain, the reaction process has not been described in detail yet.

In the present paper, we synthesized several TEA salts of phosphotungstic acid, $(\text{TEAH})_n\text{H}_{3-n}\text{PW}_{12}\text{O}_{40}$ ($n = 1, 2, 3$) by a simple acid-base reaction using a Keggin-type phosphotungstic acid and triethylamine (TEA) as raw materials. These salts were used for the selective oxidation of benzyl alcohol with the clean oxidant H_2O_2 and water as solvent. This catalytic system is environmentally friendly and exhibits high activity and selectivity. The reaction mechanism was also investigated, and a detailed process for benzyl alcohol oxidation in this system is presented.

2. Experimental

2.1. Preparation of $(\text{TEAH})_n\text{H}_{3-n}\text{PW}_{12}\text{O}_{40}$ catalysts

To an aqueous solution of 12-phosphotungstic acid was added dropwise 3 equiv. of TEA under stirring. A white precipitate appeared immediately. Stirring of the suspended solution was continued at room temperature for 24 h. The white product $(\text{TEAH})_3\text{PW}_{12}\text{O}_{40}$ was filtered out, washed with distilled water, and dried at 30 °C for 12 h. The IR characterization data were (cm^{-1}): 1079 ($\text{P}-\text{O}_a$), 979 ($\text{W}=\text{O}_d$), 896 ($\text{W}-\text{O}_b$), 810 ($\text{W}-\text{O}_c$), 1464, 1392 ($\text{C}-\text{H}$ bending), 2985 ($\text{C}-\text{H}$ stretching), and 3120 ($\text{N}-\text{H}$). The UV-Vis characterization data were (nm): 205 ($p\pi \rightarrow d\pi$ charge-transfer for $\text{O}_d \rightarrow \text{W}$) and 265 ($p\pi \rightarrow d\pi$ charge-transfer for $\text{O}_{b/c} \rightarrow \text{W}$). The ^{31}P NMR characterization data were (DMF/ D_2O , 85% H_3PO_4 as external reference): $\delta = -12.5$. The element analysis data (calcd for $\text{C}_{18}\text{H}_{48}\text{N}_3\text{PW}_{12}\text{O}_{40}$; %) were: C 6.84 (6.79); H 1.61 (1.52); N 1.50 (1.32); W 69.12 (61.30); P 0.95 (0.97).

$(\text{TEAH})_2\text{HPW}_{12}\text{O}_{40}$ and $(\text{TEAH})\text{H}_2\text{PW}_{12}\text{O}_{40}$ were prepared similarly except that the dosages of TEA were 2 and 1 equiv.,

respectively. The IR, UV-Vis and ^{31}P NMR spectra for these compounds were similar to those of $(\text{TEAH})_3\text{PW}_{12}\text{O}_{40}$. The elementary analysis data for $(\text{TEAH})_2\text{HPW}_{12}\text{O}_{40}$ (calcd for $\text{C}_{12}\text{H}_{33}\text{N}_2\text{PW}_{12}\text{O}_{40} \cdot 2\text{H}_2\text{O}$; %) were: C 4.51 (4.62); H 1.24 (1.20); N 0.79 (0.90); W 70.66 (70.74); P 0.92 (0.99), and for $(\text{TEAH})\text{H}_2\text{PW}_{12}\text{O}_{40}$ (calcd for $\text{C}_6\text{H}_{18}\text{NPW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$; %) they were: C 2.39 (2.33); H 1.04 (0.98); N 0.60 (0.45); W 71.35 (71.41); P 0.95 (1.00).

2.2. Preparation of $(\text{Bu}_4\text{N})_3(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)$ and $\text{K}_2(\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2)$

These two samples were prepared by oxidizing 12-phosphotungstic acid with 30% H_2O_2 according to the literature procedure [22]. After reacting at room temperature for 2.5 h, an aqueous solution with 3 equiv. of tetrabutylammonium chloride $((\text{Bu}_4\text{N})\text{Cl})$ was added. The resulting white $(\text{Bu}_4\text{N})_3(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)$ precipitate was filtered out, washed with water, and then dried. The IR characterization data were (cm^{-1}): 1085 ($\text{P}-\text{O}$), 1053 ($\text{P}-\text{O}$), 974 ($\text{W}=\text{O}$), 855 ($\text{O}-\text{O}$), 845 ($\text{O}-\text{O}$), 739, 650, 591 ($\text{W}(\text{O}_2)_{\text{as}}$), 575, 550, and 522 ($\text{W}(\text{O}_2)_{\text{s}}$). The UV-Vis characterization data was 248 nm, consistent with the values in Ref. [22].

Excess KCl was added to the filtrate collected in the above steps, and then ethanol was added dropwise until a white precipitate appeared. After the solution was refrigerated overnight, the precipitated $\text{K}_2(\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2)$ was filtered out, washed with ethanol and dried. The IR characterization data were (cm^{-1}): 965, 854, 835, 768, 616, and 549. The UV-Vis characterization data was 242 nm, in agreement with the results in Ref. [22].

2.3. Characterization of the samples

Infrared spectra were collected on a Bruker Tensor-27 FTIR spectrometer with a resolution of 4 cm^{-1} . Samples were prepared as KBr pellets. UV-Vis spectra of sample solutions were recorded on a Varian Cary 50 spectrophotometer with a scanning range of 200–800 nm. Element analysis for P and W was performed on a Thermo Elemental Intrepid II inductively coupled plasma-atomic emission spectroscopy (ICP-AES) instrument, and the analysis for C, H, and N was carried out on an Elementar Vario EL III instrument.

^{31}P NMR measurements were performed on a Bruker AVANCE 400 spectrometer using sample solutions with D_2O or CDCl_3 locking field. Chemical shifts were referenced to an 85% H_3PO_4 external standard. Pure POM samples were dissolved in DMF or reacted with H_2O_2 and benzyl alcohol before the measurements. The reaction solution was sampled at fixed reaction time, followed by phase separation, and then the aqueous phase and organic phase were characterized by ^{31}P NMR spectra.

2.4. Catalytic reaction

A three-neck round-bottomed flask equipped with a thermometer and a reflux condenser was charged with catalyst (0.04 mmol), 1.2 mL of 30% H_2O_2 (11.8 mmol), 1 mL of benzyl alcohol (9.6 mmol) and 10 mL of water. The system was sepa-

rated into the water-oil two phases. The catalyst was insoluble at room temperature under stirring but dissolved gradually when the system was heated to 100 °C. After reacting at this temperature for 3 h, the system was cooled to room temperature. The organic phase was extracted by acetic ether. The catalyst was precipitated on the water-oil interface and recovered by centrifugation. The extraction solution was analyzed by a SP 3400 GC apparatus equipped with a FID detector and SPB-5 capillary column (30m × 0.32mm × 1.0 μm). The yield and selectivity of the products were calculated based on the component contents analyzed using an internal standard method.

3. Results and discussion

3.1. Activity and selectivity

Except for 12-phosphotungstic acid, the catalysts in the TEA salt form were insoluble in the initial stage of the reaction, but could be dissolved during the reaction (dissolved mostly in benzaldehyde and partly in water) and extracted by adding acetic ether after the reaction. The catalytic activity, selectivity, and recovery rate of the catalysts are listed in Table 1. The conversion of benzyl alcohol was very low in the absence of the catalyst, indicating that the catalyst plays a very important role in the reaction. On all the catalysts except for $\text{H}_3\text{PW}_{12}\text{O}_{40}$, the selectivity to benzaldehyde was 100%, showing that the oxidation of benzyl alcohol to benzaldehyde was highly selective under the conditions in Table 1.

Some papers reported that increasing acidity of the reaction system was not favorable for the oxidation of alcohols [4,26]. When we added H_2SO_4 to two controlled runs using a TEA salt as the catalyst, the activity decreased (see Table 1) accompanied with the fall of the pH of the system from ~5 to 1, in accordance with the previous conclusion. However, the conversion in the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ system of high acidity was 100%, which was higher than those with the TEA salts, showing an opposite effect. This may be because $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was completely dissolved in water, resulting in full interaction with H_2O_2 so that more active species were generated. This may also be the reason for the deep oxidation of benzyl alcohol to benzoic acid and thus the lower selectivity to benzaldehyde in this system.

For three TEA salts, $(\text{TEAH})_3\text{PW}_{12}\text{O}_{40}$, $(\text{TEAH})_2\text{HPW}_{12}\text{O}_{40}$

and $(\text{TEAH})\text{H}_2\text{PW}_{12}\text{O}_{40}$, the activity increased slightly with decreasing content of TEA cations. Because of the similar acidity (pH ≈ 5 in all three systems), their difference in activity was more likely due to their solubility difference. As the TEA cations were reduced, the solubility of the catalyst in the aqueous phase increased, more active species were generated, and consequently the conversion was higher. The difference in solubility of these three catalysts can also be seen from the recovery rate of the catalysts in Table 1. The catalyst containing less TEA cations was recovered less efficiently because it dissolved in water more easily. Therefore, in this biphasic reaction, the reaction activity and selectivity could be enhanced by adjusting the content of TEA cations, which was related to the solubility of the catalyst in water and thus the yield of active species.

The catalyst in the organic phase was recovered by extraction with acetic ether, while the catalyst remaining in the aqueous phase could be reused by isolating and collecting the aqueous layer. The recovered catalyst together with the isolated aqueous layer was recycled for the oxidation of benzyl alcohol for 5 times. The activity and selectivity were basically unchanged as shown in the last two lines in Table 1, where the results in the third and the fifth cycles are given. IR spectra of the catalysts recovered after the first and the third cycles are shown in Fig. 1. The Keggin structure was found to be retained in the catalysts recovered from the organic phase by comparing their spectra with that of the fresh catalyst.

Fig. 1. IR spectra of fresh and recovered catalysts. (1) Fresh $(\text{TEAH})\text{H}_2\text{PW}_{12}\text{O}_{40}$; (2) After the 1st cycle; (3) After the 3rd cycle.

Table 1

Activity and selectivity in the oxidation of benzyl alcohol with the catalysts.

Catalyst	Conversion of benzyl alcohol (%)	Selectivity for benzaldehyde (%)	Yield of benzoic acid (%)	Recovery rate of catalyst (%)
Blank	17.9	100	0	—
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	100	92.4	7.6	0
$(\text{TEAH})_3\text{PW}_{12}\text{O}_{40}$	95.0	100	0	77
$(\text{TEAH})_3\text{PW}_{12}\text{O}_{40} + \text{H}_2\text{SO}_4^a$	84.4	100	0	62
$(\text{TEAH})_2\text{HPW}_{12}\text{O}_{40}$	97.5	100	0	58
$(\text{TEAH})\text{H}_2\text{PW}_{12}\text{O}_{40}$	99.6	100	0	53
$(\text{TEAH})\text{H}_2\text{PW}_{12}\text{O}_{40} + \text{H}_2\text{SO}_4^a$	86.7	100	0	42
$(\text{TEAH})\text{H}_2\text{PW}_{12}\text{O}_{40}$ (cycle 3)	99.8	100	0	—
$(\text{TEAH})\text{H}_2\text{PW}_{12}\text{O}_{40}$ (cycle 5)	99.5	100	0	—

Reaction conditions: catalyst 0.04 mmol, benzyl alcohol 1 mL (9.6 mmol), 30% H_2O_2 1.2 mL (11.8 mmol), H_2O 10 mL, 100 °C, 3 h.

^a H_2SO_4 (1 mol/L) was added to adjust the acidity from pH ≈ 5 to pH = 1 before heating the system.

3.2. The reaction mechanism

In previous studies on the epoxidation of olefins in a POM/H₂O₂ system [4,20–25], it was found that the POM precursor, such as PW₁₂, was first degraded to a series of undefined small peroxo active species PW_nO_x and free tungsten species when it reacted with H₂O₂. The state and concentration of the PW_nO_x species were related to the concentration of H₂O₂, reaction time and pH value of the reaction solution. The signals of the PW_nO_x in ³¹P NMR spectra shifted toward positive value with decreasing W/P ratio in the molecule, and the chemical shifts were dependent on the solvent, species concentration, cation in the phase-transfer catalyst and pH of the solution. Most of the PW_nO_x species formed in excess H₂O₂ was (PO₄(WO(O₂)₂)₄)³⁻, while the free tungsten species was (W₂O₃(O₂)₄(H₂O)₂)²⁻. After the olefin was oxidized, the peroxo species lost its active oxygen completely or partly [4,21,24,27] and was polymerized into larger stable compounds with a Keggin structure by forming intermolecular W–O–W bonds when all H₂O₂ was consumed [27].

In order to investigate the transformation of the POM species to deduce the reaction mechanism, we studied the ³¹P NMR spectra of the fresh catalyst, the catalyst reacted with H₂O₂ and the catalyst during the reaction by taking (TEAH)₃PW₁₂O₄₀ as an example. It was seen from Fig. 2 that the fresh catalyst exhibited only one peak at $\delta = -12.5$ (Fig. 2(1)), while the synthesized (Bu₄N)₃(PO₄(WO(O₂)₂)₄) showed a main peak at $\delta \approx +1.5$ (Fig. 2(2)), which was close to the previously reported value ($\delta = +1.9$) [28]. This positive shift in the chemical shift was clearly caused by the decrease of the W/P ratio in (Bu₄N)₃(PO₄(WO(O₂)₂)₄). It was also observed that more than one ³¹P line appeared in Fig. 2(2), that is, this sample was not pure. This may be due to the poor stability of (PO₄(WO(O₂)₂)₄)³⁻, which gave rise to a transformation in its

WO(O₂)₂ groups to form other PW_nO_x species [21,23,28] during the storage of the sample.

Simulating the reaction conditions, we performed the reaction of (TEAH)₃PW₁₂O₄₀ with 295 equiv. of H₂O₂ at 80 °C for 1 h. The reaction solution was examined by ³¹P NMR spectrum as shown in Fig. 2(3). The chemical shift of the main peak was close to that of (PO₄(WO(O₂)₂)₄)³⁻, meaning that this species was the main product obtained by the degradation with H₂O₂. The small shifts on both sides of the main peak were assigned to other PW_nO_x species formed during the degradation. However, when the reaction time was prolonged to 3 h (Fig. 2(4)), the (PO₄(WO(O₂)₂)₄)³⁻ species disappeared, and new peaks appeared at more positive and more negative chemical shifts, similar to the phenomenon reported in a previous study [21]. The main components in Fig. 2(4) are the species with a higher W/P ratio and even (PW₁₂O₄₀)³⁻, suggesting that the small instable peroxo species were gradually polymerized to larger species upon losing their active oxygen, or even returned to the precursor (PW₁₂O₄₀)³⁻, even though the organic substrate (benzyl alcohol) was absent and there was still H₂O₂ in the system.

In order to determine the activity of (PO₄(WO(O₂)₂)₄)³⁻ and its transformation after the reaction with benzyl alcohol, we directly used the synthesized (Bu₄N)₃(PO₄(WO(O₂)₂)₄) as the oxidant for the oxidation of benzyl alcohol in DMF. After the reaction for 3 h, benzyl alcohol had converted completely to benzaldehyde as shown by GC detection, indicating that (PO₄(WO(O₂)₂)₄)³⁻ was indeed a highly active species for alcohol oxidation. The ³¹P NMR spectra of the reaction solution are given in Fig. 2(5). A new species at $\delta \approx +2.5$ was observed accompanying the disappearance of (PO₄(WO(O₂)₂)₄)³⁻ at $\delta \approx +1.5$. This new species was generated from the reaction of (PO₄(WO(O₂)₂)₄)³⁻ with benzyl alcohol and is called a SAR (species after reaction). It would be a PW species without active oxygen or with less active oxygen because the O₂ had been transferred from (PO₄(WO(O₂)₂)₄)³⁻ to the organic substrate. This species could be polymerized into larger PW species by the formation of intermolecular W–O–W bonds [27], which gave signals with a negative chemical shift. However, there were only some very weak ³¹P signals at $\delta = -10$ to -11 (see Fig. 2(5)), suggesting that the intermolecular polymerization had not occurred to a large extent. This may be due to the absence of free tungsten species in the system and thus no tungsten source for the polymerization. Thus, it was also proposed that the polymerization involved the participation of free tungsten species.

In addition, we performed ³¹P NMR measurement for the reaction system to detect PW species formed during the reaction. After reaction for 1 and 3 h, the reaction solution was sampled, followed by water-oil separation, and then the ³¹P NMR spectra were measured for the aqueous and organic phases and are shown in Fig. 3(1)–(4). Two ³¹P peaks were observed for the aqueous phase after the reaction for 1 h, which were attributed to the SAR species and (PO₄(WO(O₂)₂)₄)³⁻, respectively, according to their chemical shifts. By comparing with Fig. 2(3), it was found that a large

Fig. 2. ³¹P NMR spectra of the catalysts. (1) (TEAH)₃PW₁₂O₄₀/DMF; (2) (Bu₄N)₃(PO₄(WO(O₂)₂)₄)/DMF; (3) (TEAH)₃PW₁₂O₄₀/DMF after reaction with H₂O₂ for 1 h; (4) (3) continued to react for another 2 h; (5) (Bu₄N)₃(PO₄(WO(O₂)₂)₄)/DMF after reaction with benzyl alcohol for 3 h. PW₁₂ = (PW₁₂O₄₀)³⁻; PW₄ = (PO₄(WO(O₂)₂)₄)³⁻.

Fig. 3. ^{31}P NMR spectra of the reaction system. (1) Aqueous phase after the reaction for 1 h; (2) Aqueous phase after the reaction for 3 h; (3) Organic phase after the reaction for 1 h; (4) Organic phase after the reaction for 3 h; (5) Aqueous phase after (1) reacting with benzyl alcohol for another 2 h; (6) Organic phase after (1) reacting with benzyl alcohol for another 2 h.

amounts of SAR species, except for $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$, were present in the system when benzyl alcohol was introduced, demonstrating that the organic substrate could effectively remove O_2 from $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ and transformed it into SAR species. In addition, although the SAR could be oxidized back to $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ in the case of H_2O_2 not being used up [21,27], the reoxidation of the SAR seemed limited here because its peak intensity was far larger than that of $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$, as shown in Fig. 3(1). When the reaction was prolonged to 3 h, only the SAR species was found in the aqueous phase (Fig. 3(2)). This was because the rate of losing the active oxygen from $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ was higher than that of the reoxidation of SAR, so $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ was transformed into SAR completely at the completion of the reaction. The ^{31}P NMR spectra for the organic phase are given in Fig. 3(3) and (4). Regardless of whether the reaction was carried out for 1 h or 3 h, there was only $(\text{PW}_{12}\text{O}_{40})^{3-}$ in the organic phase, consistent with the IR results in Fig. 1(2) and (3). These $(\text{PW}_{12}\text{O}_{40})^{3-}$ species originated from (1) the catalyst precursor dissolved in the organic layer (benzaldehyde) and unreacted with H_2O_2 ; and (2) the restored precursor regenerated by the

polymerization of the SAR with the free tungsten species and returned to the organic phase due to its being insoluble in the aqueous phase.

In order to confirm that $(\text{PW}_{12}\text{O}_{40})^{3-}$ in the organic phase was partly from the polymerization of the SAR species, we conducted two experiments as follows. (1) To the aqueous phase isolated after the reaction for 1 h (see Fig. 3(1)) was added the fresh benzyl alcohol. After running for another 2 h, the aqueous phase and the organic phase were separated again and measured by ^{31}P NMR. The results showed that there was only a small amount of SAR species in the aqueous phase (Fig. 3(5)), while $(\text{PW}_{12}\text{O}_{40})^{3-}$ was found in the organic layer (Fig. 3(6)). That is to say, the system that contained small active $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ and SAR instead of $(\text{PW}_{12}\text{O}_{40})^{3-}$ (Fig. 3(1)) could oxidize benzyl alcohol (as detected by GC) and regenerated $(\text{PW}_{12}\text{O}_{40})^{3-}$ simultaneously. This result revealed that $(\text{PW}_{12}\text{O}_{40})^{3-}$ formed in the organic phase came from the polymerization of small PW species in the aqueous phase. (2) Tungsten in the aqueous phase isolated after 1 and 3 h were analyzed by ICP-AES. The content of tungsten decreased from $35.6 \times 10^{-6} \text{ g/mL}$ (37.6% of all tungsten content in the employed catalyst) to $19.3 \times 10^{-6} \text{ g/mL}$ with the reaction progress from 1 to 3 h, giving an evidence of the transfer of PW species from the aqueous phase to the organic phase during the reaction. This transfer was a polymerization process of the small PW species to the large $(\text{PW}_{12}\text{O}_{40})^{3-}$ anion because only $(\text{PW}_{12}\text{O}_{40})^{3-}$ was detected in the organic phase.

On the other hand, the formation of free tungsten species during the reaction was also confirmed by adding KCl followed by ethanol to the aqueous phase isolated after 3 h. A white precipitate was obtained and its IR and UV-Vis spectra (omitted) were very similar to those of the synthesized $\text{K}_2(\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2)$. This species must have been involved in the polymerization of the small PW species, and as a result, the content of tungsten in the aqueous phase decreased significantly with the reaction progress.

From the above investigation and analysis, we inferred the transformation of the catalyst species and the conversion between the reactant and product as shown in Fig. 4, and deduced the reaction mechanism illustrated in Scheme 1. At the beginning of the reaction (Fig. 4(1)), the catalyst $(\text{TEAH})_3\text{PW}_{12}\text{O}_{40}$ was insoluble in the two phases, resulting in a suspension. When the temperature was increased and the reaction was pushed forward (Fig. 4(2)), part of catalyst was dissolved in the aqueous phase and interacted with H_2O_2 to degraded into the small active $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ species, which was soluble in the aqueous

Fig. 4. Transformation and distribution of the various species in the reaction system.

Scheme 1. Reaction mechanism for selective oxidation of benzyl alcohol in the $(\text{PW}_{12}\text{O}_{40})^{3-}/\text{H}_2\text{O}_2$ system.

phase but insoluble in the organic phase. Due to the considerable solubility of benzyl alcohol in water (esp. at high temperature), the oxidation of benzyl alcohol to benzaldehyde was mainly carried out in the aqueous phase. Upon reaction, $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ lost its active oxygen and was converted to the SAR. Water-insoluble benzaldehyde returned to the organic phase and dissolved unreacted $(\text{TEAH})_3\text{PW}_{12}\text{O}_{40}$ there, as measured by the ^{31}P NMR spectra (see Fig. 3(1) and (3)). Although a small amount of SAR species was reoxidized to $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ in the presence of H_2O_2 , most of these were polymerized to $(\text{PW}_{12}\text{O}_{40})^{3-}$, which was soluble in benzaldehyde. At the completion of the reaction (Fig. 4(3)), benzyl alcohol was converted to benzaldehyde almost completely, and all $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ were transformed into SAR remaining in the aqueous phase or $(\text{PW}_{12}\text{O}_{40})^{3-}$ soluble in the organic phase by the polymerization. Thus only SAR and $(\text{PW}_{12}\text{O}_{40})^{3-}$ were found in the aqueous phase and in the organic phase, respectively, as shown in Fig. 3(2) and (4). When acetic ether was added to extract the reaction solution (Fig. 4(4)), $(\text{TEAH})_3\text{PW}_{12}\text{O}_{40}$ was precipitated on the water-oil interface because it was insoluble in acetic ether. Although most of the catalyst could be recovered in the $(\text{PW}_{12}\text{O}_{40})^{3-}$ form, part of the catalyst existing in the SAR form was still left in the aqueous phase.

The above mechanism is similar to that for the Venturillo-Ishii epoxidation of olefins. However, it is different that the small active species were in the aqueous phase due to the absence of a phase transfer catalyst with a long chain, and consequently the oxidation took place in the aqueous phase. This is feasible for an alcohol soluble in water, such as benzyl alcohol, and a very high conversion can be achieved. It is the first time that the mechanism of oxidation of benzyl alcohol in $(\text{PW}_{12}\text{O}_{40})^{3-}/\text{H}_2\text{O}_2$ system is described in detail based on the ob-

servation of the SAR. It was also found that the SAR were mostly polymerized to $(\text{PW}_{12}\text{O}_{40})^{3-}$ even when H_2O_2 was not used up, which is different from the description in previous reports.

4. Conclusions

The selective oxidation of benzyl alcohol to benzaldehyde in a $(\text{PW}_{12}\text{O}_{40})^{3-}/\text{H}_2\text{O}_2$ system was investigated using $(\text{TEAH})_n\text{H}_{3-n}\text{PW}_{12}\text{O}_{40}$ ($n = 1, 2, 3$) as the catalyst. The TEA cation content could effectively regulate the solubility of the catalyst in the aqueous phase and thus the yield of the active species, resulting in improvement in activity and selectivity. The selectivity to benzaldehyde over all the TEA salt catalysts was 100%, and the conversion of benzyl alcohol over $(\text{TEAH})_2\text{PW}_{12}\text{O}_{40}$ was as high as 99%. The study on the reaction mechanism revealed that in this biphasic reaction, the catalyst and reactant species migrated and transformed constantly between the aqueous and organic phases. The catalyst first reacted with H_2O_2 and was degraded into peroxo active species $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ and free tungsten species $(\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2)^{2-}$ soluble in water. Then $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ lost its active oxygen into SAR upon the oxidation of benzyl alcohol in the aqueous phase. The SAR were polymerized with free tungsten species to form $(\text{PW}_{12}\text{O}_{40})^{3-}$, which was insoluble in water and returned to the organic phase by dissolution in benzaldehyde.

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Graphical Abstract

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Selective oxidation of benzyl alcohol catalyzed by $(\text{TEAH})_n\text{H}_{3-n}\text{PW}_{12}\text{O}_{40}$ and its reaction mechanism

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$(\text{TEAH})_n\text{H}_{3-n}\text{PW}_{12}\text{O}_{40}$ exhibited excellent catalytic performance for the selective oxidation of benzyl alcohol with hydrogen peroxide as oxidant. The reaction mechanism was investigated and described in detail.

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(TEAH)_nH_{3-n}PW₁₂O₄₀催化苯甲醇选择氧化及其反应机理

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摘要: 以Keggin结构的磷钨酸和三乙胺(TEA)为原料, 通过简单的酸碱反应合成了磷钨酸的TEA盐. 并以它们为催化剂, 考察了以H₂O₂为氧化剂、以水为溶剂的体系中苯甲醇选择氧化制备苯甲醛的反应性能. 结果表明, (TEAH)_nH_{3-n}PW₁₂O₄₀ ($n = 1, 2, 3$)系列催化剂对苯甲醇的选择氧化反应有很高的活性和选择性, 且可被分离和循环使用. 在适宜的反应条件下, 最佳催化剂(TEAH)H₂PW₁₂O₄₀上, 苯甲醇的转化率可达99.6%, 苯甲醛的选择性为100%. 还采用IR, ³¹P NMR谱和元素分析技术, 对催化剂和反应过程中催化剂物种的转化和分布进行了考察, 进而导出了反应机理. 在这个水—油两相反应中, (PW₁₂O₄₀)³⁻首先在H₂O₂的作用下, 氧化降解为溶于水的小分子过氧物种(PO₄(WO(O₂)₂)₄)³⁻和自由W物种. (PO₄(WO(O₂)₂)₄)³⁻是真正的活性物种, 可将部份溶于水层的苯甲醇氧化为苯甲醛, 自身转变为失去活性氧的反应后物种(SAR). 而SAR又可与自由W物种一起聚合为前驱体状态的(PW₁₂O₄₀)³⁻, 完成催化循环.

关键词: 苯甲醇; 选择氧化; 磷钨酸盐; 机理

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1. 前言

苯甲醛是一种非常重要的化工中间体和原料, 广泛应用于香料、农药、调味品等精细化学品的制备. 鉴于甲苯氯化水解法和甲苯氧化法等传统制备方法的诸多弊端^[1], 由苯甲醇氧化制备苯甲醛的路线受到关注^[2]. 对于苯甲醇氧化反应, 从绿色化学的角度出发, 选择价格低廉、反应条件温和、清洁环保的低浓度H₂O₂作为氧化剂无疑是一个极具竞争力的途径. 在H₂O₂参与的氧化反应中, 高效能的环境友好催化剂——多金属氧酸盐(POM)常与之组合构成POM/H₂O₂氧化体系, 并已广泛应用于烯烃环氧化^[3,4]、醇氧化^[4-6]、芳烃氧化^[7,8]等反应. 对于苯甲醇选择氧化为苯甲醛的反应, POM/H₂O₂体系

也表现出很好的催化氧化效果. 其中, 简单的水溶性POM^[9,10]在反应后不能回收, 在这个水-油两相反应中, 催化剂的循环利用是通过回收反应后的水层来实现的. 考虑到催化剂的分离回收, POM可以设计为负载型的^[11,12]或具有反应控制相转移特点^[13,14]的结构; 但反应控制相转移体系一般都要使用有机溶剂. 最近, 离子液体型POM的研究引人注目, 一些离子液体型POM^[15], 以及负载于氧化硅^[16]、介孔分子筛^[17,18]和有机聚合物^[19]上的离子液体型POM催化剂, 在苯甲醇氧化反应中也显现出很好的催化活性和循环使用性能. 但总的来说, 这些催化剂的制备一般比较复杂, 成本也较高.

关于POM/H₂O₂体系氧化机理的研究主要集中于烯烃环氧化反应, 并最早起始于以“POM/H₂O₂/相转移剂/

有机溶剂”构成的Venturello-Ishii催化氧化体系^[4,20,21]。大量研究表明, POM前驱体(PW₁₂, PMo₁₂等)与H₂O₂作用后, 首先生成过氧活性物种PX_nO_x(如(PO₄(XO(O₂)₂)₄)³⁻, X = W, Mo)^[4,20–25], 这些物种才是真正的氧化试剂。将烯烃氧化后, 催化剂又恢复PW₁₂, PMo₁₂等前驱体结构, 完成催化循环。然而, 对醇类的氧化, 反应机理的研究尚不够细致^[10,14]。Zhang等^[5]的研究表明, (PO₄(WO(O₂)₂)₄)³⁻同样是醇类氧化的活性物种, 也是检测到的唯一小分子PW物种。反应主要在油层中进行, PW₁₂与(PO₄(WO(O₂)₂)₄)³⁻间可以相互转化。然而对没有长链相转移剂参与的水-油两相中的苯甲醇氧化, 其反应过程至今未见详细描述。

鉴此, 本文以Keggin结构的钨磷酸(H₃PW₁₂O₄₀)与价格低廉的三乙胺(TEA)为原料, 通过简单的酸碱反应合成了(TEAH)_nH_{3–n}PW₁₂O₄₀ (n = 1, 2, 3), 并与绿色氧化剂H₂O₂结合用于苯甲醇的选择氧化。该催化体系具有很高的催化活性和选择性, 且反应采用水为溶剂, 避免了有机溶剂的使用, 符合绿色环保的理念。另外本文对反应机理进行了研究和探讨, 给出了在此体系中苯甲醇氧化的详细过程。

2. 实验部分

2.1. (TEAH)_nH_{3–n}PW₁₂O₄₀催化剂的制备

取一定量的磷钨酸于适量去离子水中, 搅拌至溶解。另取3倍量的TEA逐滴加入上述溶液中, 立即产生白色沉淀, 将此悬浊液在室温下搅拌24 h, 抽滤, 滤渣用去离子水洗涤数次, 30 °C干燥12 h, 得白色固体产物(TEAH)₃PW₁₂O₄₀。IR (cm⁻¹): 1079 (P–O_a), 979 (W=O_d), 896 (W–O_b), 810 (W–O_c), 1464, 1392 (C–H 弯曲), 2985 (C–H 伸缩), 3120 (N–H)。UV-Vis (nm): 205 (O_d→W的pπ→dπ电荷跃迁), 265 (O_{b/c}→W的pπ→dπ电荷跃迁)。³¹P NMR (DMF/D₂O, 85 % H₃PO₄作参比): δ = -12.5。元素分析(质量百分数(%), 括号中为理论值): C 6.84 (6.79), H 1.61 (1.52), N 1.50 (1.32), W 69.12 (61.30), P 0.95 (0.97); 对应于分子式C₁₈H₄₈N₃PW₁₂O₄₀。

(TEAH)₂HPW₁₂O₄₀和(TEAH)H₂PW₁₂O₄₀的合成方法与上相似, 只是TEA的用量分别是磷钨酸的2和1倍量。波谱表征结果也与上相似。(TEAH)₂HPW₁₂O₄₀元素分析结果: C 4.51 (4.62), H 1.24 (1.20), N 0.79 (0.90), W 70.66 (70.74), P 0.92 (0.99); 分子式为C₁₂H₃₃N₂PW₁₂O₄₀·2H₂O。(TEAH)H₂PW₁₂O₄₀的元素分析结果: C 2.39 (2.33), H 1.04 (0.98), N 0.60 (0.45), W 71.35 (71.41), P 0.95 (1.00); 分子式为C₆H₁₈NPW₁₂O₄₀·6H₂O。

2.2. (Bu₄N)₃(PO₄(WO(O₂)₂)₄)和K₂(W₂O₃(O₂)₄(H₂O)₂)的合成

此两样品系根据文献[22]方法, 用过量的30% H₂O₂氧化H₃PW₁₂O₄₀得到。室温反应2.5 h后, 加入3倍量的四丁基氯化铵((Bu₄N)Cl)水溶液。将产生的白色沉淀过滤, 收集滤液。滤渣水洗干燥后即得产物(Bu₄N)₃(PO₄(WO(O₂)₂)₄)。IR (cm⁻¹): 1085 (P–O), 1053 (P–O), 974 (W=O), 855 (O–O), 845 (O–O), 739, 650, 591(W(O₂)_{as}), 575, 550, 522 (W(O₂)_s); UV-Vis (nm): 248。与文献[22]结果一致。

滤液中加入过量KCl并摇匀使之溶解, 然后滴加乙醇直到恰好产生白色沉淀, 置于冰箱冷却过夜, 直到沉淀完全析出。滤出沉淀, 用乙醇洗涤并干燥, 得K₂(W₂O₃(O₂)₄(H₂O)₂)。IR (cm⁻¹): 965, 854, 835, 768, 616, 549; UV-Vis (nm): 242。与文献[22]结果吻合。

2.3. 样品的分析表征

IR谱在Bruker Tensor-27型红外光谱仪上测得, KBr压片, 分辨率4 cm⁻¹。UV-Vis谱在Varian Cary 50型紫外-可见分光光度计上测得, 扫描范围200~800 nm。P, W元素的分析采用Thermo Elemental Intrepid II型电感耦合等离子原子发射光谱仪(ICP-AES)进行。C, H, N元素分析采用Elementar Vario EL III元素分析仪进行。

³¹P NMR谱在Bruker AVANCE 400型核磁共振波谱仪上测得, 85% H₃PO₄作参比, D₂O或CDCl₃锁场。纯POM样品溶于DMF中进行测定, 或溶解后再与H₂O₂、苯甲醇反应以后进行测定。反应体系的测定则是将反应一定时间的溶液进行水层—油层分离, 然后分别测定水、油层。

2.4. 催化反应

在装有温度计、回流冷凝管的反应瓶中加入0.04 mmol催化剂和1.2 mL 30% H₂O₂ (11.8 mmol), 再加入1 mL苯甲醇(9.6 mmol)和10 mL H₂O, 体系分为水—油两层。室温下催化剂不溶, 搅拌下升温至100 °C, 催化剂逐渐溶解。反应3 h后冷却至室温, 用乙酸乙酯萃取反应液, 水—油界面处有催化剂析出, 离心, 分离回收催化剂。所得乙酸乙酯萃取液加内标后进行气相色谱分析。气相色谱采用SP 3400型色谱仪, 氢焰离子检测器, SPB-5毛细管柱(30 m × 0.32 mm × 1.0 μm)。采用内标法计算各组分的含量, 进而计算苯甲醇转化率、产物选择性及产率。

3. 结果与讨论

3.1. 反应活性和选择性

除磷钨酸外, 以TEA盐形式存在的催化剂在反应初期均不溶于反应体系, 但在反应过程中逐渐溶解(主要溶于生成的苯甲醛, 部分溶于水层), 并在反应后乙酸乙酯萃取过

程中被析出、回收. 表1给出了几个催化剂的催化活性、选择性和回收率. 可见, 在无催化剂的情况下, 苯甲醇的转化率很低, 表明催化剂在反应中起到了至关重要的作用. 在各催化剂中, 除 $\text{H}_3\text{PW}_{12}\text{O}_{40}$ 外, 苯甲醛选择性均达100%, 即在所用反应条件下可高选择性地实现苯甲醇的选择氧化. 有研究指出, 对于醇氧化, 体系酸度的增加不利于反应进行^[4,26]. 我们在两个使用TEA盐的反应体系中滴加 H_2SO_4 , 将体系酸度从 $\text{pH} \approx 5$ 降至1, 发现活性也有明显下降(见表1中两个加 H_2SO_4 的体系). 这说明增加体系酸度的确对反应不利. 但是强酸性的 $\text{H}_3\text{PW}_{12}\text{O}_{40}$ 的活性却略大于TEA盐的活性, 转化率高达100%, 似与上述结果不符. 这可能是因为 $\text{H}_3\text{PW}_{12}\text{O}_{40}$ 完全溶于水, 与 H_2O_2 作用更充分, 生成过氧活性物种更多的缘故. 也正因为生成的过氧活性物种太多, 导致苯甲醛深度氧化为苯甲酸, 故 $\text{H}_3\text{PW}_{12}\text{O}_{40}$ 上苯甲醛的选择性降低.

在 $(\text{TEAH})_3\text{PW}_{12}\text{O}_{40}$ 、 $(\text{TEAH})_2\text{HPW}_{12}\text{O}_{40}$ 和 $(\text{TEAH})\text{-H}_2\text{PW}_{12}\text{O}_{40}$ 三个样品中, 活性随着分子中TEA阳离子含量的减少而略有增加. 由于三者对反应体系的酸度没有明显影响(体系的 $\text{pH} \approx 5$), 所以它们不同的活性更可能来源于其溶解度的差别. 随TEA阳离子减少, 高温下催化剂在水中的溶解度逐渐增加(这也可以从表1中催化剂的回收率看出. 催化剂所含TEA离子越少, 反应后析出回收的越少, 在水层中残留的越多), 更容易与水中的 H_2O_2 反应生成活性物种, 从而有利于提高反应活性. 由此可见, 在这个水—油两相反应中, 通过调节催化剂的组成, 控制催化剂在水层中的溶解度, 可以有效控制活性物种的生成量, 提高反应的活性和选择性.

反应后经乙酸乙酯萃取, 有机层中的催化剂可以析出而回收; 存在于水层中的催化剂则可以通过分离水层而再次利用. 将回收的催化剂连同分离的水层再次用于反应, 重复循环5次, 活性和选择性基本不变. 表1最后两行给出了循环第3次和第5次的反应结果. 第1次和第3次循环后催化剂的IR谱示于图1. 可见, 回收催化剂的IR谱与新鲜催化剂的IR谱完全一致. 表明有机层中的催化剂不仅性能稳定, 而且保持了Keggin单元和结构.

3.2. 反应机理研究

POM/ H_2O_2 体系中烯烃环氧化的研究表明, PW_{12} 等POM前驱体遇 H_2O_2 后首先发生降解, 生成一系列不确定的小分子过氧活性物种 PW_nO_x 和不含P的自由W物种^[4,20–25]. 其中 PW_nO_x 物种的形态及浓度大小与 H_2O_2 的浓度、反应时间以及溶液的 pH 有关. 它们在 ^{31}P NMR谱上的信号随W/P比的下降而移向正值, 且

化学位移取决于溶剂、物种浓度、相转移剂阳离子、以及 pH 等因素. 在过量 H_2O_2 存在下生成的 PW_nO_x 物种主要是 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$, 而自由W物种则是 $(\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2)^{2-}$ ^[21,22]. 活性物种将烯烃氧化后, 自身失去或部分失去活性氧^[4,21,24,27], 并在 H_2O_2 消耗完后通过形成分子间W—O—W键重新聚合为更稳定的Keggin结构化合物^[27].

为了考察反应过程中POM物种的变化, 以导出反应机理, 本文以 $(\text{TEAH})_3\text{PW}_{12}\text{O}_{40}$ 样品为例, 用 ^{31}P NMR研究了新鲜催化剂、催化剂+ H_2O_2 、以及催化剂在反应体系中的存在状态. 由图2可见, 新鲜的 $(\text{TEAH})_3\text{PW}_{12}\text{O}_{40}$ 催化剂只有一个 $\delta = -12.5$ 的谱峰(图2(1)). 我们合成的 $(\text{Bu}_4\text{N})_3(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)$ 样品的谱峰则移至 $\delta \approx +1.5$ 处(图2(2)), 与文献[28]报道的化学位移值($\delta = +1.9$)接近. 这一移动是由于其W/P比降低所致. 然而, 图2(2)的 ^{31}P 信号不止一个, 表明该样品不纯净, 可能是 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 的稳定性差, 在存储过程中过氧物种中的 $\text{WO}(\text{O}_2)_2$ 基团容易变化^[21,23,28], 转化为其它 PW_nO_x 物种所致.

模拟反应条件, 我们将 $(\text{TEAH})_3\text{PW}_{12}\text{O}_{40}$ 催化剂与295倍量的 H_2O_2 在80 °C反应1 h, 所得溶液的 ^{31}P NMR示于图2(3). 可见, 主峰的位置与 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 接近, 表明催化剂被 H_2O_2 降解后主要生成 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 物种, 而主峰两侧的其它小峰则是降解过程中生成的其它 PW_nO_x 物种. 然而当反应时间延长至3 h时(图2(4)), $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 物种消失, 在正、负值方向出现新的谱峰, 与文献[21]报道的现象相似. 尤其是图2(4)的主要组分是W/P较高的物种, 且出现了 $(\text{PW}_{12}\text{O}_{40})^{3-}$ 的谱峰, 表明即使在没有反应底物(苯甲醇)存在、体系中仍有 H_2O_2 的情形下, 小分子过氧物种也会由于自身的不稳定, 逐步失去活性氧并聚集成高W/P比的物种, 甚至恢复前驱体 $(\text{PW}_{12}\text{O}_{40})^{3-}$ 的状态.

为了考察 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 物种的活性以及与苯甲醇反应后物种的变化, 我们将合成的 $(\text{Bu}_4\text{N})_3(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)$ 直接作为氧化剂, 在DMF中单独与苯甲醇进行反应. 反应3 h后经GC检测, 苯甲醇已全部转化为苯甲醛, 说明 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 的确是高活性的醇氧化物种. 反应溶液的 ^{31}P NMR谱示于图2(5). 可见, 反应后位于 $\delta \approx +1.5$ 附近的 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 物种消失, 却出现了 $\delta \approx +2.5$ 物种. 显然, 该物种是 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 与苯甲醇反应后生成的物种(我们称之为反应后物种(SAR)), 它极可能是 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 将活性氧转移给有机底物后

生成的不含活性氧或含较少活性氧的PW物种. 这种物种可通过形成分子间的W–O–W键, 聚集成大的PW物种^[27], 并在负 δ 值方向出现信号. 然而图2(5)仅在 $\delta = -10 \sim -11$ 处出现一些很弱的³¹P峰, 说明分子间的聚合并未大量发生. 这应该是体系中没有自由W物种, 聚合因缺乏W源而不能进行的缘故. 反之这也说明分子间的聚合涉及自由W物种的参与.

我们进而对反应过程中的PW物种进行了检测. 将反应1 h和3 h后的反应液进行水层-油层分离, 分别检测其³¹P NMR谱, 所得结果示于图3(1)~(4). 1 h的水层中检测到两个³¹P谱峰(图3(1)), 由其化学位移值可知, 它们分别对应于SAR物种和 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$. 与图2(3)相比, 在有苯甲醇参与的情况下, 体系中除有 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 物种外, 还有大量的SAR物种, 表明反应底物能及时有效地移去 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 中的 O_2 , 将其转化为SAR. 另外, 尽管在 H_2O_2 没有耗尽的情况下, SAR可被再次氧化为 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ ^[21,27], 但两峰中前者的强度远大于后者, 表明SAR被再次氧化的量是有限的. 3 h水层的³¹P NMR谱示于图3(2). 可以看出, 此时只有SAR物种. 这是因为 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 失去活性氧的速度远大于SAR被再次氧化的速度, 所以 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 最终全部转化为SAR. 图3(3)和(4)则给出了油层中的情况. 可见, 不论是1 h还是3 h, 油层中都只有 $(\text{PW}_{12}\text{O}_{40})^{3-}$ 物种, 与图1(2)和(3)所示的从油层中回收的催化剂的IR结果一致. 这些 $(\text{PW}_{12}\text{O}_{40})^{3-}$ 物种来源于: (1)溶于油层(苯甲醛)中的尚未与 H_2O_2 作用的催化剂前驱体; (2) SAR物种与自由W物种一起重新聚合为低温下难溶于水的催化剂前驱体, 并溶于油层.

为了证实油层中的 $(\text{PW}_{12}\text{O}_{40})^{3-}$ 部分来源于小SAR物种的聚合转化, 我们做了两个实验. (1)将反应1 h后分出的水层(图3(1))添加新鲜的苯甲醇继续反应2 h, 反应完成后分离水层和油层, 用³¹P NMR分别检测其中的物种. 结果显示, 水层中只有少量的SAR物种(图3(5)), 而油层中检测到 $(\text{PW}_{12}\text{O}_{40})^{3-}$ 物种(图3(6)). 即, 含活性 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 和SAR等小PW物种而不含 $(\text{PW}_{12}\text{O}_{40})^{3-}$ 的体系(图3(1))可将新鲜苯甲醇氧化(GC检测证实), 同时生成 $(\text{PW}_{12}\text{O}_{40})^{3-}$. 这表明生成的 $(\text{PW}_{12}\text{O}_{40})^{3-}$ 来源于原体系中小PW物种的聚合. (2)我们对反应1 h和3 h水层中的W含量作了元素分析, 结果表明, 随反应进行, 水层中的W含量减少, 由1 h的 $35.6 \times 10^{-6} \text{ g/mL}$ (约占投入催化剂总W量的37.6%)变为3 h的 $19.3 \times 10^{-6} \text{ g/mL}$. 这表明在反应过程中水层中的PW物

种向油层中转移. 由于油层中只检测到 $(\text{PW}_{12}\text{O}_{40})^{3-}$, 所以这一转移是水层中小PW物种聚合为 $(\text{PW}_{12}\text{O}_{40})^{3-}$ 的过程.

另一方面, 我们在反应3 h后的水层中加入少许KCl, 再加乙醇, 可以析出白色沉淀. 此沉淀的IR、UV-Vis谱(略)与我们合成的 $\text{K}_2(\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2)$ 的相应谱图非常相似, 表明反应过程中也生成了自由W物种 $(\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2)^{2-}$. 而小分子的PW物种聚合恢复为 $(\text{PW}_{12}\text{O}_{40})^{3-}$ 的过程也一定涉及这些自由W物种, 从而导致水层中W含量大大降低.

由上面的考察和分析, 我们可以推断反应过程中反应物和产物、以及POM催化剂物种间的转化关系(图4), 并给出反应机理(式1). 反应初始(图4(1)), 催化剂 $(\text{TEAH})_3\text{PW}_{12}\text{O}_{40}$ 不溶于有机层和水层, 呈悬浊液. 随温度的升高和反应的进行(图4(2)), 部分催化剂溶于水并与水层中的 H_2O_2 作用, 降解成小分子活性物种 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$. 这样的小分子物种溶于水层, 不溶于油层; 而苯甲醇在水中也有相当的溶解度(尤其在高温下), 因此苯甲醇转化为苯甲醛的反应主要在水层中进行. 反应后, $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 失去活性氧转变为SAR物种; 而不溶于水的苯甲醛又回到油层, 并将未反应的 $(\text{TEAH})_3\text{PW}_{12}\text{O}_{40}$ 溶解到油层中, 正如³¹P NMR(图3(1)和(3))检测到的那样. 在 H_2O_2 的作用下, 尽管小部分SAR物种可被其重新氧化为 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$, 但大部分SAR物种聚合为 $(\text{PW}_{12}\text{O}_{40})^{3-}$, 并溶于苯甲醛(油层)中. 随着反应的继续进行(图4(3)), 苯甲醇几乎完全转化为苯甲醛, 水层中的 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 也全部转化为SAR, 或经SAR聚合为 $(\text{PW}_{12}\text{O}_{40})^{3-}$ 而回到油层. 所以水层中只检测到SAR, 油层中则只有 $(\text{PW}_{12}\text{O}_{40})^{3-}$, 如图3(2)和(4)所示. 反应后(图4(4)), 当加入乙酸乙酯萃取反应混合物时, $(\text{TEAH})_3\text{PW}_{12}\text{O}_{40}$ 由于不溶于乙酸乙酯而在水-油界面上析出. 尽管大部分催化剂最终可以 $(\text{PW}_{12}\text{O}_{40})^{3-}$ 的状态被回收, 但水层中仍残留部分以SAR状态存在的催化剂物种.

上述机理与Venturello-Ishii体系中烯烃的环氧化机理非常相似, 不同的是, 由于没有长链相转移剂存在, 小分子活性物种处于水层, 氧化反应须在水层中进行. 这对于在水中有相当溶解度的醇类(例如苯甲醇)来说, 反应可以进行, 并有很高的活性. 另外, 本文首次在醇类的氧化反应中检测到SAR物种, 对 $(\text{PW}_{12}\text{O}_{40})^{3-}/\text{H}_2\text{O}_2$ 体系中苯甲醇的氧化机理进行了比较详细的描述, 并发现SAR主要转化为 $(\text{PW}_{12}\text{O}_{40})^{3-}$, 即

使在 H_2O_2 没有耗尽的情况下也是如此,这与以往的机理描述有所不同.

4. 结论

采用磷钨酸的三乙胺盐 $(\text{TEAH})_n\text{H}_{3-n}\text{PW}_{12}\text{O}_{40}$ ($n = 1, 2, 3$)为催化剂,对苯甲醇选择氧化为苯甲醛的反应进行了考察.改变TEA离子的引入量,可以有效调节催化剂在水层中的溶解度,控制活性物种的生成量,从而提高反应的活性和选择性.所有 $(\text{TEAH})_n\text{H}_{3-n}\text{PW}_{12}\text{O}_{40}$ 催化剂

上苯甲醛的选择性均为100%.其中, $(\text{TEAH})\text{H}_2\text{PW}_{12}\text{O}_{40}$ 上苯甲醇转化率高达99%以上.对反应机理的研究显示,反应中催化剂物种和反应物种在水—油两相中不断地迁移和转化.催化剂首先与水层中的 H_2O_2 作用,降解为溶于水的过氧活性物种 $(\text{PO}_4(\text{WO}(\text{O}_2)_2)_4)^{3-}$ 和自由W物种 $(\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2)^{2-}$,然后在水层中将溶于水的苯甲醇氧化,自身失去活性氧转化为SAR物种;SAR物种又与自由W物种一起,聚合为难溶于水的 $(\text{PW}_{12}\text{O}_{40})^{3-}$ 并回到油层.