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Selective Oxidation of Benzyl Alcohol by Heteropolytungstate as Reaction-Controlled Phase-Transfer Catalyst with Hydrogen Peroxide

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The catalytic oxidation of benzyl alcohol to benzaldehyde was studied using heteropolytungstates as reaction-controlled phase-transfer catalysts with 35% aqueous H_2O_2 as oxidant. Under optimal conditions, 95.0% conversion of benzyl alcohol based on H_2O_2 and over 99% selectivity of benzaldehyde was obtained with $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$ as catalyst. In this system, once the H_2O_2 was consumed, the catalyst could be recovered from the system easily as a solid deposit. The catalysts were characterized by FT-IR, ^{31}P NMR, XRD, and TGA, and the results indicated that the insoluble catalyst $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$ formed a soluble active species $[C_7H_7N(CH_3)_3]_3[(PO_4)\{WO(O_2)_2\}_4]$ under the action of H_2O_2; the structure of the fresh catalyst was maintained well after the reaction. The results of catalyst recycling showed that this catalyst exhibits good stability. The effects of various reaction factors, such as solvent and the amount of H_2O_2 used, were studied.

The selective oxidation of alcohols to the corresponding aldehydes is an important transformation in organic synthesis.[1,2] Thus, there have been hundreds of publications emphasizing environmentally benign methods utilizing molecular oxygen or H_2O_2 as oxidants. Although catalytic aerobic oxidation is certainly of importance, H_2O_2-mediated oxidations also possess many crucial advantages, such as high oxygen availability and good oxidizing power. Up to now, many catalytic systems have been reported in the area of oxidation of benzyl alcohol (BzOH) to benzaldehyde (PhCHO) with H_2O_2 as oxidant.[3–9] Among them, heteropolyoxometalates as homogeneous catalysts have attracted much attention particularly in the last two decades,[10–13] and some good results have been obtained.

The dearth of these homogeneous catalysts can be attributed to the difficult separation of catalyst from product and invariable chromatographic procedure for recovery of the catalyst. It would be very advantageous for practical and industrial application if the catalyst could be easily separated from the reaction solution by precipitation. The setup of Xi's[14] reaction-controlled phase-transfer catalytic system can be amenable to this type of catalyst. The solubility of his catalyst $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{16}]$ in the reaction solution could be controlled by its reaction with H_2O_2. It could dissolve into the reaction medium under the action of H_2O_2, and then precipitate from the solvent after the oxidation reaction was over (H_2O_2 was consumed). To the best of our knowledge, reports on the oxidation of BzOH with H_2O_2 in the presence of reaction-controlled phase-transfer catalysts are few. We have reported a reusable heteropolyoxometalate $[C_7H_7N(CH_3)_3]_3PMo_4O_{24}$ which successfully catalyzed the selective oxidation of BzOH to PhCHO using H_2O_2 as an oxidizing agent.[15,16] Herein, we synthesized a series of heteropolytungstates to screen another effective new catalyst for this oxidative system.

Experimental

Unless specially mentioned, the reagents used in this work were at least C.P. grade and were used as supplied.

Preparation of Catalysts. $Na_8HPW_9O_{34}\cdot 24H_2O$ was synthesized according to the method reported by Richard et al.[17] The 2.848 g (1 mmol) of $Na_8HPW_9O_{34}\cdot 24H_2O$ obtained was dissolved in 100 mL of distilled water at 60 °C with stirring, followed by addition of 1.857 g (10 mmol) of solid benzyltrimethylammonium chloride to the colorless solution. The resulting reaction mixture was stirred at 60 °C for another 30 min. The precipitate, being the product $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$ ($Q_9PW_9O_{34}$), was filtered, successively washed with water and diethyl ether, and dried under infrared light. Found: C, 29.45; H, 4.11; N, 3.61; P, 0.81; W, 45.37%. Calcd for $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$: C, 30.16; H, 4.02; N, 3.52; P, 0.87; W, 46.24%.

General Procedure of Catalytic Oxidation Reaction. A three-necked round-bottom flask equipped with a reflux condenser and thermometer was charged with catalyst, 35% aqueous H_2O_2, and alcohol in a molar ratio of 1:225:250, and finally 10 mL of dimethylacetamide (DMAc) as solvent. The reaction mixture was stirred at 80 °C for a determined time. Then, the reaction mixture was cooled down to room temperature. The precipitate catalyst was separated by centrifugation. The organic phase was analyzed by GC with an internal standard. Unless otherwise mentioned, conversion is based on H_2O_2.

Characterization of Catalyst. Elemental analysis of the catalyst was carried out with a varioEL III (made by Elementar Company) and by ICP-atomic emission spectroscopy (Optima 2000DV). Infrared spectra were recorded on a Nicolet-20DXB FT-IR spectrometer in KBr disks at room temperature. ^{31}P NMR was recorded on a Varian UNITY INOVA 400 spectrometer. The spectra of catalysts in solvents were obtained with a D_2O internal tube for field locking. The ^{31}P chemical shifts were referenced to 85% H_3PO_4 aqueous solution. Powder X-ray diffraction experiments were conducted on a Rigaku D/max-2400 diffraction

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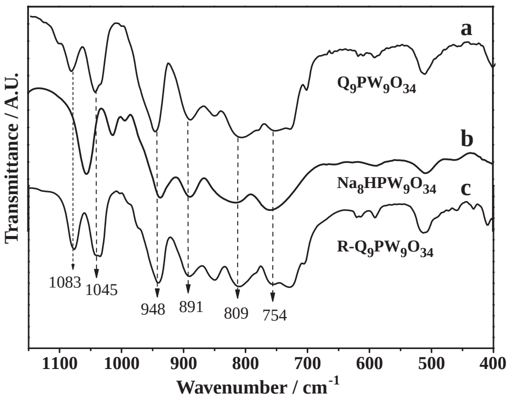

Figure 1. FT-IR spectra of catalysts.

instrument using Cu Kα radiation at a wavelength of 0.15406 nm. A scan rate of 0.15° s^{-1} with a step size of 0.02° was used for data collection. Thermal stabilities of the catalysts were examined by performing thermogravimetry analyses (TGAs) on a NETZSCH TGA 209 instrument, thermal scanning was done at temperatures ranging from 25 to 550 °C at a heating rate of 10 °C min^{-1}.

Results and Discussion

Catalyst Characterization. Figure 1 shows FT-IR spectra of the starting material $Na_8HPW_9O_{34}$, and both fresh and recovered $Q_9PW_9O_{34}$. The IR spectrum of fresh $Q_9PW_9O_{34}$ exhibited characteristic peaks at 1083–1045, 948, 891, and 809–754 cm^{-1} which could be attributed to ν(P–O), ν(W=O), ν(W–O$_b$–W), and ν(W–O$_c$–W), respectively. Compared to the absorption peaks of $Na_8HPW_9O_{34}$ at 1055–1013, 936, 889, and 815–759 cm^{-1}, obvious changes of peaks in the ν(P–O) region were observed. The ν(P–O) peaks at 1055 and 1013 cm^{-1} in $Na_8HPW_9O_{34}$ shifted to the longer wavenumber region 1083 and 1045 cm^{-1} in $Q_9PW_9O_{34}$, and the other peaks of ν(W=O), ν(W–O$_b$–W), and ν(W–O$_c$–W) stayed almost the same. There was no obvious difference between the IR spectra of the recovered (Figure 1c) and fresh catalyst. These results confirmed that the structure of fresh catalyst was maintained well after the reaction.

^{31}P NMR spectra of catalysts are shown in Figure 2. The chemical shifts of fresh and recovered $Q_9PW_9O_{34}$ in dimethyl sulfoxide (DMSO) appear at −9.4 and −9.6 ppm, respectively. When insoluble fresh and recovered catalysts were treated with H_2O_2 in DMAc, their spectra both exhibited only one peak at 3.1 ppm indicating that the recovered catalyst formed the same structure as the fresh during the oxidation reaction. The line at 3.1 ppm can be attributed to $[(PO_4)\{WO(O_2)_2\}_4]^{3-}$.[18–20] These results showed that after it reacted with H_2O_2, the catalyst depolymerized into a smaller active species which was soluble in the reaction medium; when the oxidant H_2O_2 was consumed, the soluble species polymerized into insoluble larger compounds with Keggin-structure framework.[21]

Figure 3 shows the XRD patterns of fresh and recovered $Q_9PW_9O_{34}$ ($5° \leqslant 2\theta \leqslant 80°$). For these two catalysts, the peaks of X-ray diffraction mostly lay in four regions, where 2θ is 6–7, 16–18, 20–23, and 24–27°, and the peak at 6.84° was the most intense ($d = 12.912$ Å). However, for recovered catalyst, a high intense peak appearing at 20.94° ($d = 4.239$ Å) may be attributed to rearrangement of the counter cation of the catalyst. These indicated that the structures of the catalysts are maintained well after reaction.

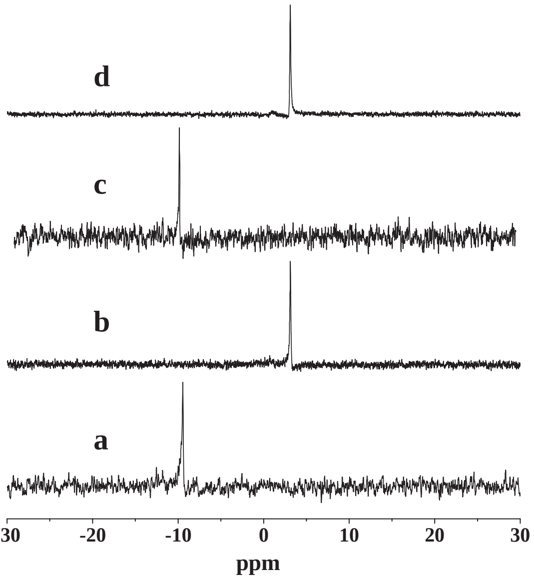

Figure 2. ^{31}P NMR spectra of catalysts.

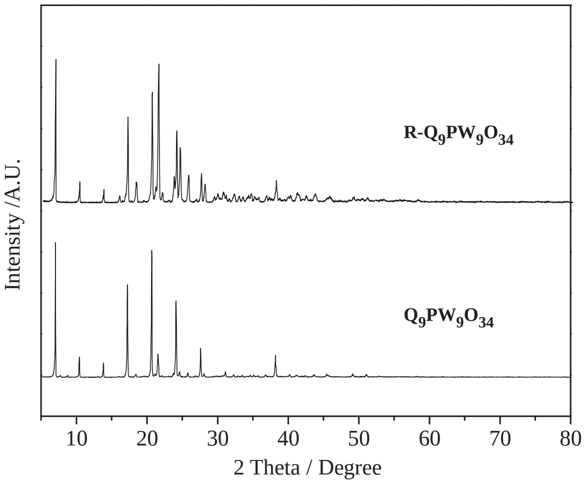

Figure 3. X-ray diffraction of the $Q_9PW_9O_{34}$ and recovered $Q_9PW_9O_{34}$.

The thermal stabilities of $Q_9PW_9O_{34}$ and recovered $Q_9PW_9O_{34}$ were determined by TGA. The curves of representative samples are shown in Figure 4. It can easily be surmised from the two types of curves that the samples had three weight loss steps in the 25–550 °C temperature range. For $Q_9PW_9O_{34}$, the first weight loss step occurred at 100 °C, and the corresponding weight loss was 21.8% being close to the weight loss and the calculated value of 23.6% for the loss of the benzyl group of the counter cation. The second weight loss between 186 and 256 °C could be ascribed to the decomposition of the quaternary ammonium group. The last weight loss from 420 °C can be attributed to decomposition of the structure of the $[PW_9O_{34}]^{9-}$ anion. For recovered $Q_9PW_9O_{34}$, the shape of the curve was similar to that of fresh $Q_9PW_9O_{34}$, however, the residual weight of the former was a little higher than that of the latter. This result indicated that a small part of organic counter cation of the catalyst was lost after reaction.

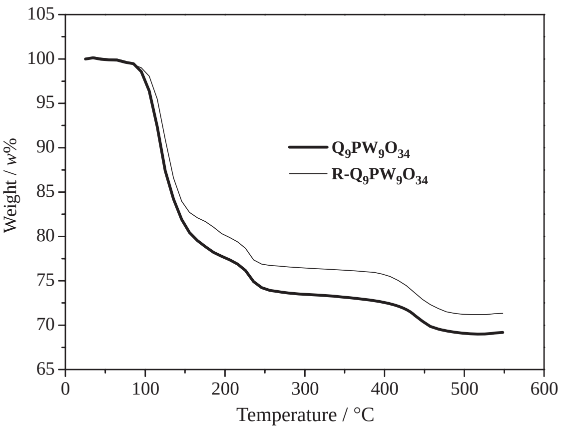

Figure 4. TGA curves of $Q_9PW_9O_{34}$ and recovered $Q_9PW_9O_{34}$.

Catalytic Performance. In order to compare the activities of oxidation of BzOH by various catalysts, three other catalysts $Q_3PW_{12}O_{40}$, $Q_3PMo_{12}O_{40}$, and $Q_3PMo_4O_{24}$ (Q^+ represents $[C_7H_7N(CH_3)_3]^+$) were employed in this reaction. As shown in Table 1, no feature of the reaction-controlled phase-transfer catalysis appeared in the systems with $Q_3PW_{12}O_{40}$ and $Q_3PMo_{12}O_{40}$ as catalyst, the catalysts were still soluble in the solvent within the determined reaction time, and the reaction conversions were poor (38.5% and 24.6%, respectively). For $Q_9PW_9O_{34}$ and $Q_3PMo_4O_{24}$, the resulting catalysts demonstrated a dissolving–precipitating phenomenon, they exhibited good activities in the oxidation of BzOH to PhCOH (the conversions were 95.0% and 92.8%, respectively), and no by-products were detected by GC. However, the $Q_9PW_9O_{34}$ was much more efficient than $Q_3PMo_4O_{24}$; their TOF were 428 and 60 h^{-1}, respectively. Compared to the system with several novel kinds of bis-quaternary phosphonium salts of peroxotungstate and peroxomolybdate as catalysts reported by Shi and Wei[13] (93.9% yield of PhCHO was obtained at 80 °C for 8 h), our system showed higher activity. In order to vividly describe the process of the reaction-controlled phase-transfer catalysis, pictures of the reaction mixture at different stages are shown in Figure 5. Before H_2O_2 was added to the reaction system, the white $Q_9PW_9O_{34}$ powders were insoluble in the reaction solvent (Figure 5a). At the beginning of the reaction, the catalyst dissolved quickly in the solvent with magnetic stirring. As shown in Figure 5b the reaction solution was clear, leaving only the magnetic stirring bar visible at the bottom of flask, and the $Q_9PW_9O_{34}$ acted as homogeneous catalyst during the reaction. Once the H_2O_2 was consumed, the catalyst precipitate appeared in the bottom of the flask (Figure 5c), and could be easily recovered by filtration.

The solvent plays a key role in reaction-controlled phase-transfer catalytic systems. In dissimilar solvents, the catalysts show different phenomenon during the reaction. Herein, we chose various solvents to explore their effects on the catalytic system. In the catalytic system with $[C_7H_7N(CH_3)_3]^+$ as counter cation, the solvents were screened as shown in Table 2. Toluene, 1,2-dichloroethane (DCE), and tributyl phosphate (TBP) were not suitable solvents for this oxidation system due to the insolubility of the catalyst in the reaction medium in spite of reacting with H_2O_2. In these heterogeneous catalytic systems, conversions of BzOH were poor within the given reaction time. This catalyst was soluble in acetonitrile, dimethylformamide (DMF), and DMAc in the present of H_2O_2, and with the increase of polarity of the solvents (acetonitrile < DMF < DMAc), the conversion of BzOH increased from 65.2% to 95.0%. However, the catalyst was still soluble in DMF after the H_2O_2 was used up. Although the catalyst recovery ratio in acetonitrile (92.3%) was a little higher than that in DMAc (88.1%), the conversion of BzOH in the former system was almost 30% lower than that in the latter. Thus, DMAc was the best reaction solvent in this catalytic system.

The effect of the amount of H_2O_2 on the oxidation of BzOH is presented in Table 3. When the molar ratio of H_2O_2 to BzOH was increased from 0.3 to 0.9, the conversion of BzOH was found to dramatically increase from 16.5% to 85.5% with

Table 1. Catalytic Oxidation of BzOH by Various Heteropolyoxometalates with H_2O_2

Catalyst	Solvent	Time/h	Solubility of catalyst		Conversion/%	TON[a)]	TOF[b)]/h^{-1}
			During reaction	After reaction			
$Q_3PW_{12}O_{40}$	DMAc	3.5	soluble	soluble	38.5	87	25
$Q_9PW_9O_{34}$	DMAc	0.5	soluble	insoluble	95.0	214	428
$Q_3PMo_{12}O_{40}$	acetonitrile	3.5	soluble	soluble	24.6	55	16
$Q_3PMo_4O_{24}$	acetonitrile	3.5	soluble	insoluble	92.8	209	60

a) Turnover number calculated as products (mmol)/catalyst (mmol). b) Turnover frequency calculated as TON/Time (h).

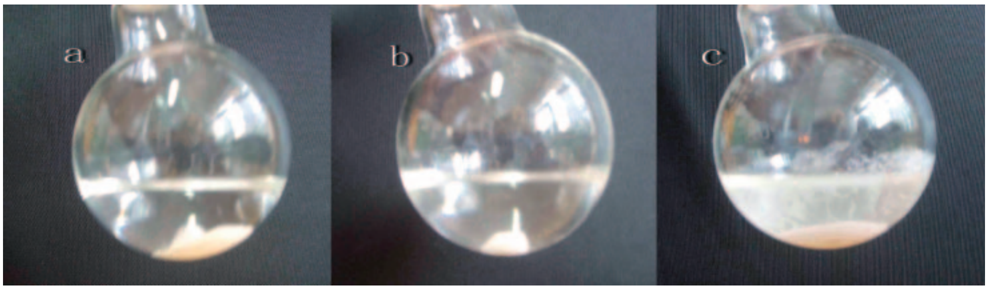

Figure 5. Pictures of the process of the reaction.

Table 2. Effect of Solvent on System with BTMA as Counter Cation

Solvent	Time /h	Solubility of catalyst		Conversion /%	Catalyst recovery ratio/wt %
		During reaction	After reaction		
Toluene	3	insoluble	insoluble	14.2	—[a)]
DCE	3	insoluble	insoluble	25.9	—[a)]
TBP	3	insoluble	insoluble	17.0	—[a)]
Acetonitrile	0.5	soluble	insoluble	65.2	92.3
DMF	3	soluble	soluble	74.3	—[a)]
DMAc	0.5	soluble	insoluble	95.0	88.1

a) The catalyst was insoluble during the reaction, under this condition, the reaction was not completed.

Table 3. Effect of H_2O_2 to BzOH Molar Ratio on the Oxidation of BzOH

H_2O_2/BzOH	Time/h	Conversion/%[a)]	Selectivity/%	
			PhCHO	PhCOOH
0.3	0.5	16.5	$\geq$99	—[b)]
0.9	0.5	85.5	$\geq$99	—[b)]
1	1	89.4	$\geq$99	—[b)]
1.25	3	93.2	96.4	3.7
1.5	5	100	86.7	13.3

a) The conversion is based on BzOH. b) Under these conditions, there was no PhCOOH detected by GC.

excellent selectivity (no benzoic acid (PhCOOH) was detected by GC). When H_2O_2/BzOH ratio was 1.5 and the reaction time prolonged to 5 h, complete conversion of BzOH (100%) was obtained, however, with the sacrifice of the selectivity. Therefore, from the point of view of oxidative selectivity, H_2O_2 was used as the limiting oxidant reactant in order to minimize the formation of PhCOOH. However, the dissolving–precipitating circulation of the catalyst was controlled by the reaction between catalyst and H_2O_2. From Table 3, we can see the optimum H_2O_2/BzOH was 1.

It would be preferable for industrial manufacturers for the catalyst to be reused as many times as possible. We explored the recycle-number of our catalyst. The recovered catalyst by centrifugation was reused under the same reaction conditions as the fresh. In the subsequent test, for maintaining the same amount of the catalyst as the first run, a little fresh catalyst was added to the recovered catalyst. As shown in Figure 6, although the catalyst was recycled three times, there was no obvious lower conversion of BzOH as well as catalyst recovery ratio. These results revealed that our catalyst had stable catalytic activity in the recycle.

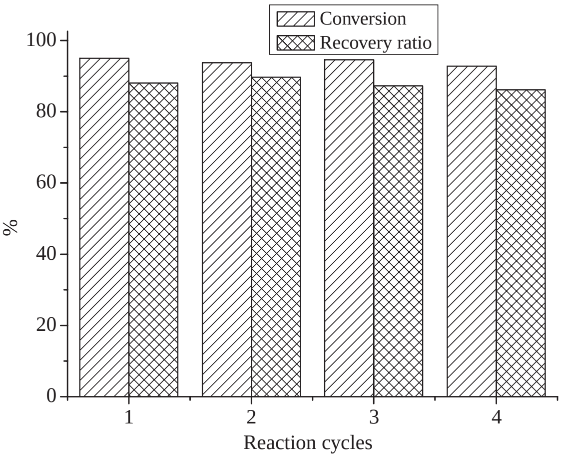

Figure 6. The results of recycling of the catalyst.

Conclusion

An investigation was carried out for the use of some heteropolytungstate catalysts in the oxidation of BzOH to PhCHO with H_2O_2 as oxidizing agent. It was confirmed that $[C_7H_7N(CH_3)_3]_9[PW_9O_{34}]$ showed the expected feature of reaction-controlled phase-transfer catalysis and had the highest activity (the conversion was 95.0% based on H_2O_2) in the reaction. When the H_2O_2 was completely consumed, the catalyst precipitated from the reaction medium and could be easily separated from the reaction system by centrifugation. The catalyst could be recycled three times without decreasing the catalytic activity and the recovery ratio of catalyst. The effects of reaction parameters were discussed. The primary analytic results indicated that $Q_9PW_9O_{34}$ formed active species $Q_3[(PO_4)\{WO(O_2)_2\}_4]$ during the reaction and the small species polymerized into the insoluble $Q_9PW_9O_{34}$ once the H_2O_2 was used up. Investigation of the detailed mechanism of benzyl alcohol oxidation in this catalytic system is underway.

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