On the nature of reaction-controlled phase transfer catalysts for epoxidation of olefin: a ^{31}P NMR investigation

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$[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ was reported to be an excellent epoxidation catalyst which exhibited a unique reaction-controlled phase transfer behavior. In the paper, the composition and structural changes of the reaction-controlled phase transfer catalyst during and after reaction have been investigated by ^{31}P NMR spectroscopy. The ^{31}P MAS NMR confirmed that the original catalyst was a mixture of heteropoly tungstophosphates. When the catalyst reacted with hydrogen peroxide, the species $\{PO_4[WO(O_2)_2]_4\}^{3-}$, $[(PO_4)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$ and $[(PO_3(OH))\{WO(O_2)_2\}_2]^{2-}$ were detected by *in situ* ^{31}P NMR. It was also found that the P/W ratios and quaternary ammonium cations had great influence on the composition of heteropoly tungstophosphates. Although the catalyst with $[(C_{18}H_{37})_2N(CH_3)_2]^+$ was not a reaction-controlled phase transfer catalyst, it could be precipitated from the reaction solution when acetone was subsequently added to the solution. The ^{31}P MAS NMR spectra of the recovered catalysts revealed that they had more low P/W ratio heteropoly tungstophosphates than fresh catalysts.

KEY WORDS: reaction-controlled phase transfer; epoxidation; ^{31}P NMR; heteropoly tungstophosphates.

1. Introduction

The alkene epoxidations have been studied for many years on both industrial and laboratory scale. Especially, the catalytic epoxidation of olefins using environmentally benign oxidant, such as O_2 and H_2O_2, has attracted more and more attention in recent years [1]. Heteropoly oxometalates as well as simple materials containing molybdenum and tungsten are identified to be effective homogeneous catalyst for olefin epoxidation [2]. In past decades, the extensively studied epoxidation system relevant to heteropoly tungstophosphates was venturllo-Ishii system, in which the epoxidations of olefins were catalyzed by $Q_3\{PO_4[WO(O_2)_2]_4\}^{3-}$ ($Q =$ quaternary ammonium ion) and $Hn[XM_{12}O_{40}]$ ($X = P, Si; M = Mo, W$) with dilute hydrogen peroxide as oxidant under phase-transfer conditions [3–5]. In spite of good activity and selectivity of the heteropoly oxometalates, the catalysts are difficult to be separated from the products. In order to solve this problem, heterogenization of such catalysts has been studied in many ways [6–8]. Recently, Xi *et al.* reported on reaction-controlled phase transfer catalysis for epoxidation of olefins with H_2O_2 generated *in situ* or commercially available 30% H_2O_2 as the oxidant [9,10]. In their process, the insoluble catalyst $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3$-$[PW_4O_{16}]$ formed soluble active species by the action of H_2O_2 initially, and when the H_2O_2 was used up, the catalyst precipitated for easy recycling (scheme 1). However, the authors just assigned the molecular formula $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ according to elemental analysis and drew a conclusion that the recovered catalyst was the same as original catalyst by FT-IR characterization.

^{31}P MAS NMR spectroscopy is a powerful tool to characterize the phosphorous-containing solid catalyst [11,12]. In the present paper, we report on the ^{31}P NMR spectroscopic investigation of the composition of the catalyst $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ and its compositional change during and after reaction. Moreover, the influence of the P/W ratios and the quaternary ammonium cations on the composition of this kind of heteropoly tungstophosphates is studied.

2. Experimental

Unless specially mentioned, the reagents used in the work were of C.P. grade and were used without further purification.

2.1. Preparation of catalysts

The catalyst $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ was prepared by the method described in literature [13]. A suspension of tungstic acid (2.50 g, 10 mmol) in 7 mL of 35% aqueous H_2O_2 was heated to 60 °C and stirred for 15 min. Forty percent H_3PO_4 (0.62 mL, 2.5 mmol; H_3PO_4:$H_2WO_4 = 1:4$) was added to the obtained colorless solution at room temperature (about 25 °C) and the whole solution was diluted with another 20 mL of water and then stirred for 30 min. To the resultant solution, 1.80 g of cetylpyridinium chloride (CPC)

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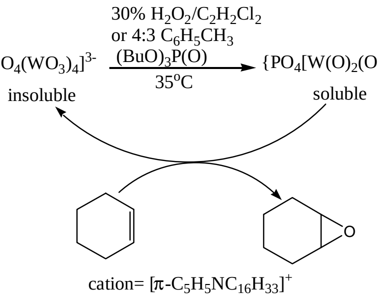

Scheme 1. The process of reaction-controlled phase transfer catalysis for epoxidation of olefin.

(5 mmol) in dichloromethane (40 mL) were added dropwise with stirring. After the solution was stirred continuously for 30 min, the organic phase was separated, dried over anhydrous Na_2SO_4, filtered and then the solvent was removed at 60 °C under atmospheric pressure. A yellow dry powder was obtained by further evaporating under reduced pressure.

The catalysts with P/W ratio of 1/3, 1/2 were prepared replacing H_3PO_4 with $NaH_2PO_4 \cdot 2H_2O$ and Na_2HPO_4, respectively.

The catalysts with different quaternary ammonium cations were synthesized with dioctadecyl dimethyl ammonium chloride ($(C_{18}H_{37})_2N(CH_3)_2Cl$), hexadecyl trimethyl ammonium chloride ($C_{16}H_{33}N(CH_3)_3Cl$) and benzyl trimethyl ammonium chloride ($C_6H_5CH_2\text{-}N(CH_3)_3Cl$) (all C.P. grade and purchased from Qingpu Reagent Plant, China).

2.2. Biphasic catalytic epoxidation of cyclohexene

The reaction was carried out, in air and under 1 atm pressure, in a glass reactor system in a water bath and stirred with a magnetic stir bar. To a solution of the catalyst (0.1 g) and 35% H_2O_2 (8.0 mmol) in $C_2H_4Cl_2$ (8 mL) was added the cyclohexene (16.0 mmol), and the mixture was maintained at 55 °C with vigorous stirring for 4 h. After the reaction, the resultant organic layer was analyzed by GC with an internal standard technique. The catalyst was recovered by a simple filtration and dried in air.

2.3. ^{31}P MAS NMR and *in situ* ^{31}P NMR measurements of the catalysts

The NMR spectra were recorded at 9.4 T on a Bruker DRX 400 NMR spectrometer. The ^{31}P MAS NMR spectra of solid catalysts with high-power proton decoupling were performed at 161.9 MHz with BBO MAS probehead using 4 mm ZrO_2 rotors and 2.0 μs pulse, 2 s repetition time and 2048 scans, with samples spun at 8 kHz. The ^{31}P NMR spectra of catalysts in solvents were obtained with BBI 5 mm inverse broadband probehead with D_2O internal tube for locking field. The ^{31}P chemical shifts were referenced to 85% H_3PO_4 aqueous solution.

2.4. IR characterization of catalysts

Infrared spectra were recorded on a Nicolet Impact 410 FT-IR spectrometer. The catalysts were measured using 2–4% (w/w) KBr pellets prepared by manual grinding.

3. Results and discussion

3.1. Fresh catalysts

The ^{31}P MAS NMR spectrum of $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ (denoted PW_4) is shown in figure 1a. The broad peak from 0 to −15.0 ppm can be assigned to heteropoly tungstophosphates with the ratio of P/W from 1/2 to 1/12 [14]. The species at about 6.1 and

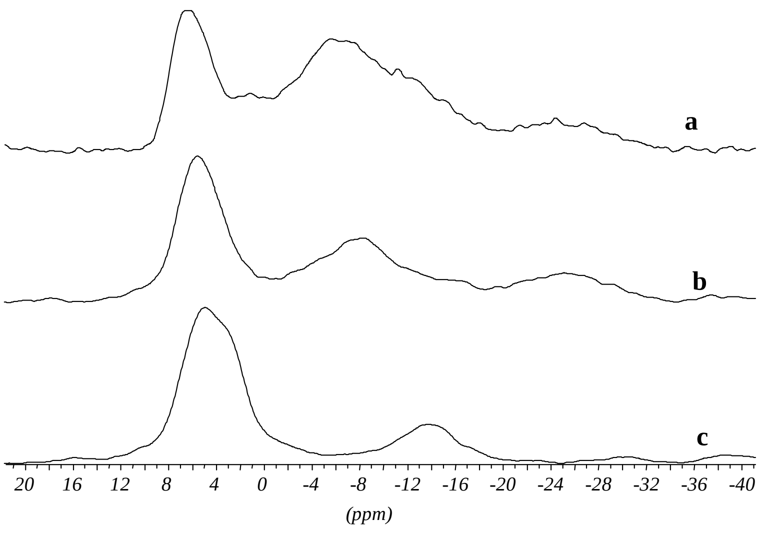

Figure 1. ^{31}P MAS NMR spectra of catalysts prepared with different P/W ratio. (a) PW_4; (b) PW_3; (c) PW_2.

−25.5 ppm might be due to species with higher P/W ratio and species with lower P/W ratio, respectively. It is clear that $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ is not pure but consists of many components. With the increasing P/W ratio (1/3,1/2 denoted PW_3,PW_2), the relative intensities of peaks around −10.0 and −25.5 ppm decrease (figure 1b) or disappear (figure 1c), i.e. the relatively pure catalyst can be got with higher P/W ratio. The IR spectra (not shown here) of these catalysts show no peak at 840 cm^{-1} (attributed to –O–O– stretching vibration) [15,16], which indicates that the catalysts mentioned above do not contain active oxygen.

The catalysts with different P/W ratios were tested for epoxidation of cyclohexene using 35% aqueous hydrogen peroxide as oxidant. Table 1 lists the results of epoxidation of cyclohexene catalyzed by these catalysts. The conversions of cyclohexene can reach to 98% and 100%, respectively, and the selectivity for epoxide is higher than 90%. The turnover numbers (TON) of the catalysts are 130, 155 and 156, and the H_2O_2 efficiency for epoxide is around 90%. At the end of the reaction, it was found that the catalysts PW_3, PW_2 and PW_4 all precipitated from the reaction media. The catalysts recovered amounted to 55%, 60% and 83% (w/w) of the catalysts added, respectively. That is to say, although the catalysts with different P/W ratios can exhibit the characteristics of reaction-controlled phase transfer catalysis, the P/W ratios influence the recovery of catalysts. The results can be explained by following *in situ* ^{31}P NMR spectroscopy of these catalysts in the presence of H_2O_2.

3.2. Catalysts in the presence of H_2O_2

Figure 2 shows the ^{31}P NMR spectra of the catalysts (PW_4, PW_3 and PW_2) in CH_2Cl_2 after reacted with H_2O_2. The peaks at 4.1, 0.3 and −1.5 ppm correspond to $\{PO_4[WO(O_2)_2]_4\}^{3-}$, $[(PO_4)\{WO(O_2)_2\}\{WO(O_2)_2(H_2O)\}]^{3-}$ and $[(PO_3(OH))\{WO(O_2)_2\}_2]^{2-}$, respectively [17,18]. In the IR spectra of the reaction solution, the –O–O– stretching vibration at 840 cm^{-1} are observed, which supports that catalysts with active oxygen are formed in the presence of H_2O_2. These active-oxygen-containing species have been regarded as real oxidant, since they all can be used as stoichiometric oxidant for epoxidation of alkenes to epoxides [19]. The peak at −2.5 ppm is identified unambiguously as cetylpyridinium phosphate $[[\pi\text{-}C_5H_5NC_{16}H_{33}]_3PO_4$, $[\pi\text{-}C_5H_5NC_{16}H_{33}]_7PW_{11}O_{39}$, $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3\,PW_{12}O_{40}$ were synthesized and characterized by ^{31}P NMR spectroscopy in our lab]. which

Table 1
Epoxidation of cyclohexene with 35% H_2O_2 by catalysts with different P/W ratio

Catalyst	P/W	Conversion[a] (%)	Selectivity (%)	TON[b]	H_2O_2 efficiency (%)	Recycle yield of cat. (%)
PW_2	1/2	98	90	130	88	55
PW_3	1/3	98	96	155	94	60
PW_4	1/4	100	93	156	93	83

[a] Conversion of cyclohexene was based on H_2O_2.

[b] TON = turnover number, TON was based on cyclohexene oxide.

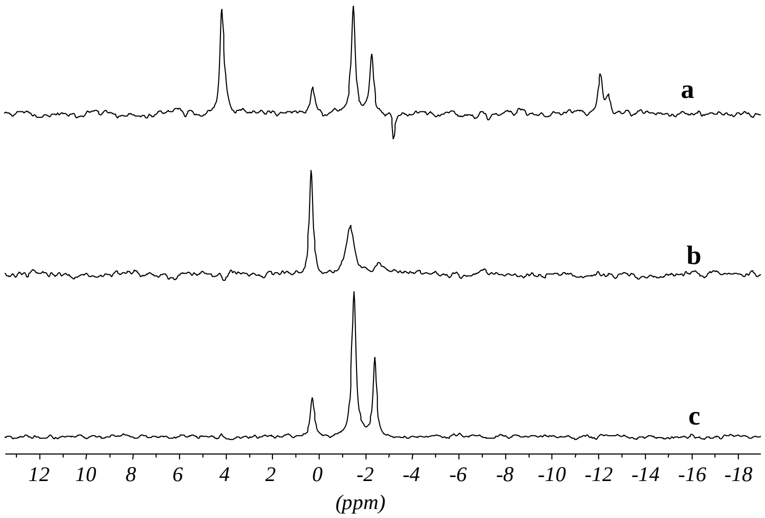

Figure 2. ^{31}P NMR spectra of catalysts in CH_2Cl_2 after reaction with 35% H_2O_2. (a) PW_4; (b) PW_3; (c) PW_2.

might come from two sources: (1) From the procedure of preparation of catalysts. When the catalysts were prepared through distilling CH_2Cl_2, the cetylpyridinium phosphate would partly remain in the solid phase. (2) From the reaction course of catalysts with H_2O_2. When the species with higher ratio of P/W were transformed to lower ratio of P/W species with active oxygen, the residue of phosphorous would form cetylpyridinium phosphate. The peak at about −12.1 ppm is due to some undissociated polyanions (PW_{12} and PW_{11}) which can react with H_2O_2 to form the active species mentioned above [15,17]. Only the catalyst $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ has the peak at 4.1 ppm, which proves that the catalyst contain more tungsten atoms than the other catalysts (PW_3 and PW_2), since the peaks attributed to $[(PO_4)\{WO(O_2)_2\}\{WO(O_2)_2(H_2O)\}]^{3-}$ and $[(PO_3(OH))\{WO(O_2)_2\}_2]^{2-}$ are the strongest for PW_3 and PW_2, respectively. In combination with the catalytic results (table 1), we think $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is the most active species and easily precipitated from reaction solution after active oxygen lost.

Species $[(PO_4)\{WO(O_2)_2\}\{WO(O_2)_2(H_2O)\}]^{3-}$ and $[(PO_3(OH))\{WO(O_2)_2\}_2]^{2-}$ are also detected in water when the catalysts reacted with H_2O_2. The solubility of these species in water made the recovery yield of PW_2 and PW_3 low.

3.3. Recovered catalysts

The ^{31}P MAS NMR spectra of the recovered catalysts are shown in figure 3. Compared with the spectra of fresh catalysts, it is found that the relative intensity of peak at higher fields (from −13.1 to −15.6 ppm) increase for recovered catalysts, which indicates the formation of species with lower P/W ratios. For the catalyst $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ recovered from the $C_3H_6/C_6H_5CH_3/(C_4H_9O)_3PO/H_2O_2$ generated *in situ* system, the intensity of the peaks at −13.1 ppm increase and separate from other peaks (figure 3b), while the catalyst recovered from $C_6H_{10}/C_2H_4Cl_2$/35% H_2O_2 system has only the signal at −13.1 ppm (figure 3a). The spectrum of fresh PW_2 catalyst shows little signal at −13.1 ppm (figure 3e). However in the spectra of recovered catalysts (figure 3c and d), the intensities of the signals around −13.1 ppm are strong. The peaks at −13.1 and −15.6 ppm are attributed to $(PW_{11}O_{39})^{7-}$ and $(PW_{12}O_{40})^{3-}$ with Keggin structure, respectively [$[\pi\text{-}C_5H_5NC_{16}H_{33}]_3PO_4$, $[\pi\text{-}C_5H_5NC_{16}H_{33}]_7PW_{11}O_{39}$, $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3$ $PW_{12}O_{40}$ were synthesized and characterized by ^{31}P NMR spectroscopy in our lab]. The spectra of catalysts recovered from C_3H_6 system (figures 3b and c) exhibited a sharp peak at about −1.0 ppm which might be assigned to $(P_4W_8O_{40})^{12-}$ [14]. For the recovered catalysts, the proportion of lower P/W ratio species increases relative to fresh catalyst. These results reveal

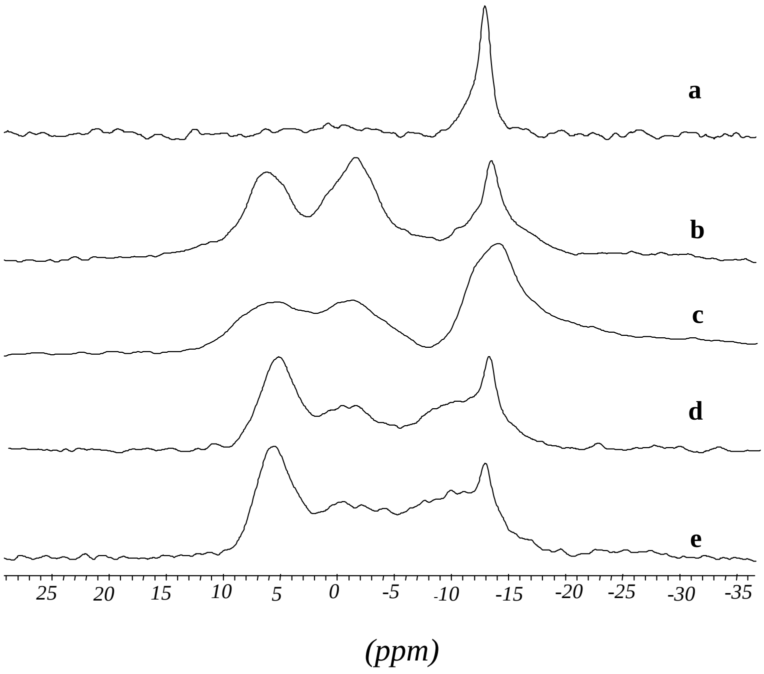

Figure 3. ^{31}P MAS NMR spectra of recovered catalysts. (a) PW_4 ($C_6H_{10}/C_2H_4Cl_2$/35% H_2O_2); (b) PW_4 ($C_3H_6/C_6H_5CH_3/(C_4H_9O)_3PO/H_2O_2$ generated *in situ* by 2-ethylanthraquinone(EAQ) and 2-ethylanthrahydroquinone (EAHQ)); (c) PW_2 ($C_3H_6/C_6H_5CH_3/(C_4H_9O)_3PO$/50% H_2O_2); (d) PW_2 ($C_6H_{10}/C_2H_4Cl_2$/cat/35% H_2O_2); (e) PW_3 (C_6H_{10} /$C_2H_4Cl_2$/cat/35% H_2O_2). Reaction conditions: (a), (d) and (e) see experimental Section 2.2. (b) 75.0 mL of hydrogenation solution (EAHQ) was oxidized with O_2; C_3H_6:EAHQ:Cat = 750:300:1(molar ratio): reaction temperature and time: 65 °C, 5 h; catalyst recovery 75%; more detailed information see [9]. (c) Solvent: $C_6H_5CH_3:(C_4H_9O)_3PO = 4:3$; $C_3H_6:H_2O_2$ (50%): Cat = 700:300:1(molar ratio): reaction temperature and time: 65 °C, 5 h; catalyst recovery 78%.

that the solvent system as well as substrate has influence on the structure of recovered catalysts to some extent. That is, all the free H_2O_2 as well as the active oxygen of catalysts are consumed, and the catalysts would self-assemble to form species with lower P/W ratio. With the above results in hand, we tried to use directly $Q_7(PW_{11}O_{39})$ and $Q_3(PW_{12}O_{40})$ ($Q = \pi\text{-}C_5H_5NC_{16}H_{33}$) as the catalysts for epoxidation of olefin. The results showed that the catalytic efficiency was much less than that of catalysts we have synthesized. Meanwhile, it took a longer time for the compounds of PW_{11}, PW_{12} to dissolve in the solvent. We propose that the species with higher P/W ratio are easier to react with H_2O_2 than $Q_7(PW_{11}O_{39})$ and $Q_3(PW_{12}O_{40})$.

3.4. Catalysts with different cations

Xi *et al.* have reported that the cations played an important role in reaction-controlled phase transfer catalytic epoxidation, namely, the choice of appropriate countercations is very crucial for the precipitation of heteropoly species from the reaction media [9,10]. Another three catalysts with different cations, $[(C_{18}H_{37})_2N(CH_3)_2]^+$, $[C_{16}H_{33}N(CH_3)_3]^+$ and $[C_6H_5\text{-}CH_2N(CH_3)_3]^+$ were synthesized (denoted Cat-$C_{18\text{-}3}$, Cat-$C_{16\text{-}3}$, and Cat-$C_{6\text{-}3}$). It was found that only the Cat-$C_{16\text{-}3}$ also exhibited the characteristic of reaction-controlled phase transfer catalysis.

Figure 4 shows ^{31}P MAS NMR spectra of catalysts with different cations mentioned above. For catalyst Cat-$C_{18\text{-}3}$, there is a main peak at 2.8 ppm, and its IR spectra (figure 5c) gives a strong peak at 840 cm^{-1}, which indicates that the catalyst still contain active oxygen. While peaks mainly at −13.0 and −15.5 ppm due to $(PW_{11}O_{39})^{7-}$ and $(PW_{12}O_{40})^{3-}$ are observed in the ^{31}P MAS NMR spectrum of Cat-$C_{6\text{-}3}$, which means that small species had aggregated to form compounds with Keggin structure in preparation process. Its IR spectrum (figure 5d) is a mixture of that of $(PW_{11}O_{39})^{7-}$ and $(PW_{12}O_{40})^{3-}$ (1077 cm^{-1} $\nu(PO_4)$; 967 cm^{-1} $\nu(W{=}O)$; 880 cm^{-1} $\nu(W\text{–}O_b\text{–}W)$; 813 cm^{-1} $\nu(W\text{–}O_c\text{–}W)$). Although the intensity around 10 ppm is obviously different in ^{31}P MAS NMR spectra of Cat-$C_{16\text{-}3}$ and $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$, the active species $\{PO_4[WO(O_2)_2]_4\}^{3-}$, $[(PO_4)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$, $[(PO_3(OH))\{WO(O_2)_2\}_2]^{2-}$ are detected simultaneously in reaction solution, and the IR spectra of fresh catalysts showed almost no active oxygen (figure 5a and b). So the type of quaternary ammonium cation affects the composition of this kind of catalyst, and bigger cation can efficiently stabilize active oxygen.

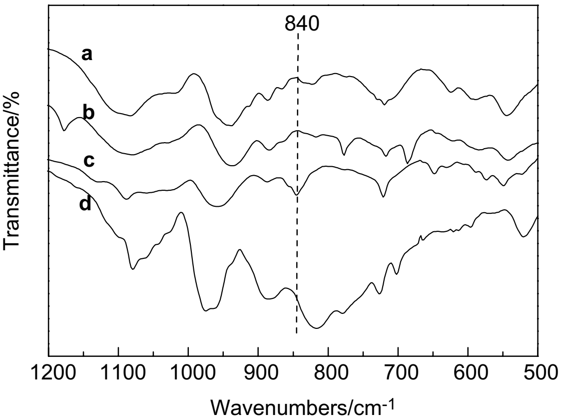

Figure 5. IR spectra of the catalysts with different cations. (a) $[C_{16}H_{33}N(CH_3)_3]^+$; (b) $[\pi\text{-}C_5H_5NC_{16}H_{33}]^+$; (c) $[(C_{18}H_{37})_2N(CH_3)_2]^+$; (d) $[C_6H_5CH_3N(CH_3)_3]^+$.

When the cation is $[(C_{18}H_{37})_2N(CH_3)_2]^+$ with two longer fatty acid chains, the catalyst is still dissolvable in reaction solution after reaction. It was interesting that

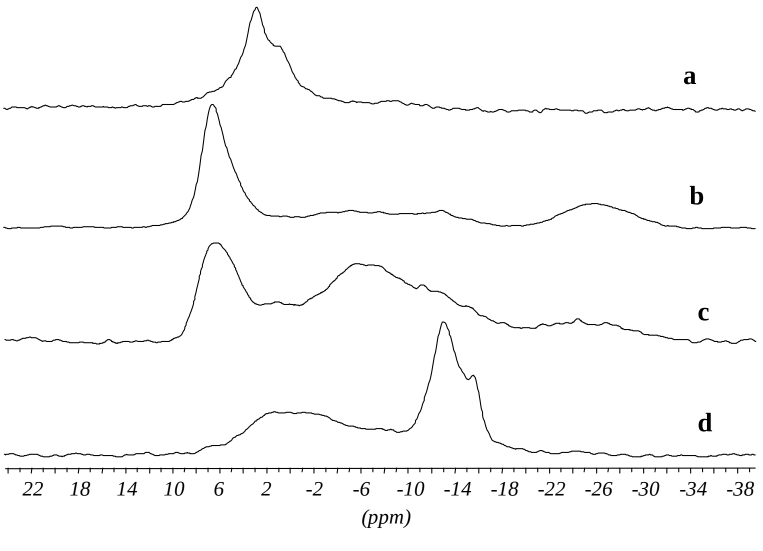

Figure 4. ^{31}P MAS NMR spectra of catalysts with different cation. (a) $[(C_{18}H_{37})_2N(CH_3)_2]^+$ (Cat-$C_{18\text{-}3}$); (b) $[C_{16}H_{33}N(CH_3)_3]^+$ (Cat-$C_{16\text{-}3}$); (c) $[\pi\text{-}C_5H_5NC_{16}H_{33}]^+$; (d) $[C_6H_5CH_3N(CH_3)_3]^+$ (Cat-$C_{6\text{-}3}$).

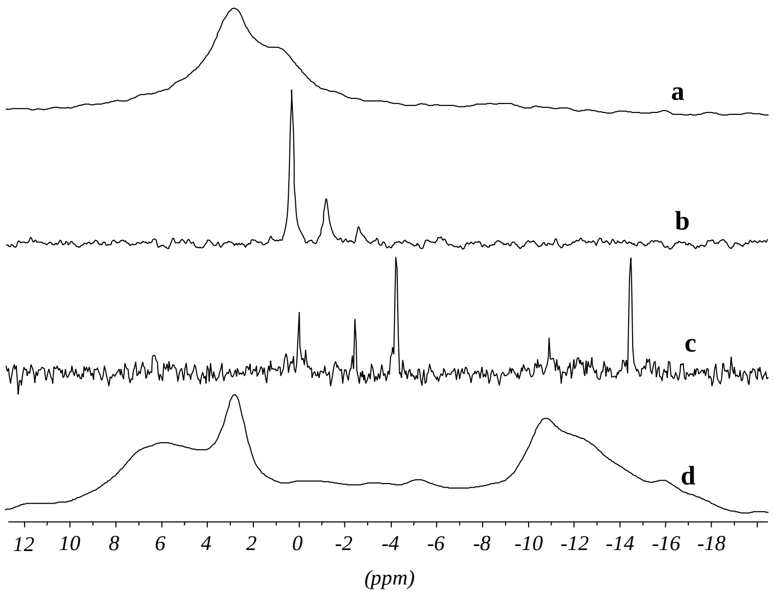

Figure 6. ^{31}P NMR spectra of the catalyst with $[(C_{18}H_{37})_2N(CH_3)_2]^+$ in different states: (a) fresh catalyst; (b) during epoxidation process; (c) after reaction; (d) recovered catalyst.

when the catalyst Cat-C_{18-3} was used, by adding acetone to the reaction solution (about 4:1 V/V) after the reaction, part of catalyst precipitated and the recover efficiency of the used catalyst was 40% or higher. The change process of Cat-C_{18-3} was monitored by ^{31}P NMR measurements (figure 6). The fresh catalyst Cat-C_{18-3} is constituted of higher P/W ratio heteropol tungstophosphates. When it react with H_2O_2, the active species mainly $[(PO_4)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$ and $[(PO_3(OH))\{WO(O_2)_2\}_2]^{2-}$ are observed. After reaction, although it still dissolved in solution, heteropoly tungstophosphates with low P/W ratio ($PW_{12}O_{40}{}^{3-}$) appear, which is in agreement with the recovered catalyst.

4. Conclusions

The reaction-controlled phase transfer catalyst $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ is a mixture of heteropoly tungstophosphates. When the catalyst react with H_2O_2, species $(PO_4)\{WO(O_2)_2\}_4]^{3-}$, $[(PO_4)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$, $[(PO_3(OH))\{WO(O_2)_2\}_2]^{2-}$ are formed. The P/W ratio and the type of quaternary ammonium cation in preparation process have great impact on the composition of heteropoly tungstophosphates. Although the catalyst with $[(C_{18}H_{37})_2N(CH_3)_2]^+$ is not reaction-controlled phase transfer catalyst, it precipitate after acetone is added to the reaction solution subsequently. After the reaction, parts species of high P/W ratio in fresh catalyst change to species of low P/W ratio. The ^{31}P NMR method is very effective for revealing the structural changes and the phase-transfer behaviors of the catalysts during the reaction process.

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