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Influence of composition of heteropolyphosphatotungstate catalyst on epoxidation of propylene

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Abstract

A series of heteropolyphosphatotungstate catalysts with different *W*/*P* ratio were prepared by different means. ^{31}P MAS NMR spectra show every heteropolyphosphatotungstate contains several species with different *W*/*P* ratio. Combined with propylene epoxidation results, it is shown that the band at chemical shift ca. $\delta = 5$ ppm maybe corresponds to a catalyst precursor which can be the most efficiently converted to the structure $\{PO_4[WO(O_2)_2]_4\}^{3-}$. Characterization results of ICP show, the catalysts with low *W*/*P* ratio show a good reactivity for propylene epoxidation.

Keywords: Propylene; Epoxidation; Heteropolyphosphatotungstate

1. Introduction

Alkenes epoxidation is a class of very important reactions. In 1983, Venturello et al. [1,2] proposed that the complex consisting of tungstate and phosphate can catalyze the epoxidation of different alkenes with dilute H_2O_2 solution (15%) as oxidant. In 1988, Ishii et al. [3] proposed that the system composed of $H_3PW_{12}O_{40}$ and cetylpyridinium chloride can catalyze epoxidation of alkenes with commercially available H_2O_2 solution as oxidant. Xi et al. [4] proposed a new concept of "reaction controlled phase transfer catalyst". This class of heteropolyphosphatotungstate catalysts can dissolve into the reaction system upon the interaction with H_2O_2, catalyze epoxidation of alkenes; while H_2O_2 is used up, these catalysts can precipitate from reaction system, thus the recycling problem of homogeneous catalyst is solved. Especially for propylene, these catalysts take on a prospect of industrial application. But the mechanism of the catalyst $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ is not very clear. In this respect, Aubry et al. [5] demonstrated that upon the interaction with excess H_2O_2, $H_3PW_{12}O_{40}$ will degrade into several species containing tungsten include $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ and $\{PO_4[WO(O_2)_2]_4\}^{3-}$, only $\{PO_4[WO(O_2)_2]_4\}^{3-}$ can be transferred into organic phase under the condition of phase transfer, so very probably $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is the active center. Duncan et al. [6] confirmed this hypothesis by a study on the mechanism and dynamics of epoxidation reaction. They proposed that $PO_4[WO(O_2)_2]_4{}^{3-}$ is the active intermediate in the Ishii–Venturello system. While reacting with 1-octene, the intermediate will be transformed into a mixture of three polytungstatophosphate: PW_4, PW_3, PW_2; which are called "subsequent peroxo species" (SPS), and be regenerated to $\{PO_4[WO(O_2)_2]_4\}^{3-}$ structure again upon the interaction with H_2O_2. The crystals of $\{HPO_4[WO(O_2)_2]_2\}^{2-}$ [7] and $\{PO_4[WO(O_2)_2]_4\}^{3-}$ [8] were prepared and investigated. In the two phase epoxidation of limonene by H_2O_2, tungsten species $Q_3\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $Q_2\{HPO_4[WO(O_2)_2]_2\}^{2-}$ proved to be 30 times more active than the molybdenum analog [7]. Melaine Gresley et al. also reported their studies on the nature of $\{PO_4[WO(O_2)_2]_2[WO(O_2)_2(H_2O)]\}^{3-}$ [9]. Salles et al. [10] pointed out that there is a dynamic equilibrium in the $\{PO_4[WO(O_2)_2]_4\}^{3-}$ structure, the position of four WO $(O_2)_2$ structure units in $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is exchangeable. Based on research results mentioned above, with the purpose to look for catalysts more suitable to the application of propylene epoxidation, clarify the functions of the content of tungsten and phosphate, a series of

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heteropolyphosphatotungstates were prepared, their structure were characterized with FT-IR ICP and ^{31}P MAS NMR, their reactivity for propylene epoxidation was investigated.

2. Experimental

2.1. Preparation of catalyst

2.1.1. Catalyst A series

The catalyst A $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ was prepared according to Sun et al. [11]. By the same means, except the cetylpyridinium chloride was replaced by cetyltrimethyl ammonium chloride, catalyst AT was obtained.

2.1.2. Catalyst C

The preparation procedure of catalyst C was similar with catalyst A. But in the step of extraction of $\{PO_4[WO(O_2)_2]_4\}^{3-}$, the quaternary ammonium salt was replaced by $(C_{18}H_{37}\ (30\%) + C_{16}H_{33}(70\%)))N^+(CH_3)_3Cl^-$ with a molar ratio $PO_4{}^{3-}/Q^+$ of 1:3, and the solvent was replaced by CH_2ClCH_2Cl. In the course of stirring, the catalyst C was precipitated. The catalyst was washed by water until the pH of washed liquid was 4, dried under the infrared light.

2.1.3. Catalyst B, D and insoluble B

The catalysts B and D were prepared by the means similar to catalyst C. The catalyst “insoluble B” was obtained by a modification to catalyst B. Catalyst B was stirred 40 min at ambient temperature in 0.3 M H_2O_2 solution resulting from oxidation of 2-ethylanthrahydroquinone in trimethyl benzene (TMB) and tributyl phosphate (TBP) mixed solvent, then the suspension was filtered. Obtained solid was washed by toluene, dried under the Infrared light.

2.2. Catalytic reaction of propylene epoxidation

A 0.3 M 2-ethylanthrahydroquinone solution (TMB/TBP mixed solvent) was taken and oxidized with 1 atm O_2 in a water bath at 35 °C, then in situ H_2O_2 solution was obtained, the concentration of H_2O_2 was titrated by $KMnO_4$ solution. 50 ml in situ H_2O_2 solution was taken and put into a glassy lining, with the total amount of H_2O_2 worked out. The catalyst was added into the lining based on the ratio of 0.015 mol H_2O_2:0.1g catalyst and a quantity of benzene were added as the internal standard. The lining was put into a 200 ml stainless steel autoclave. Propylene was charged into the autoclave, then discharged into atmosphere, such operation was repeated three times. After that 2.65 g propylene was charged into autoclave. The reaction was carried out in a water bath at 65 °C for 5 h. When the reaction was over, the autoclave was cooled to ambient temperature. The amount of propylene oxide was analyzed on a HP 4890 gas chromatograph with the internal standard method.

2.3. Soluble behavior test

Soluble behavior test of catalysts was performed on a 250 ml conical flask filled with a certain amount of in situ H_2O_2 solution. The catalyst A or B was put into the conical flask with a ratio of 0.015 mol H_2O_2:0.1 g catalyst. Then the conical flask was put into a water bath at 65 °C, magnetically stirred about 2 h, testifying whether the two catalysts are soluble.

2.4. Characterization of catalyst

2.4.1. FT-IR spectra

Infrared spectra was recorded on a NEXUS 470 FT-IR spectrometer. The catalysts were measured using 2–4% (w/w) KBr pellets and prepared by manual grinding using a mortar and pestle.

2.4.2. ICP

ICP was performed on Atom Scan Advantage spectrometer.

2.4.3. ^{31}P MAS NMR spectra

The ^{31}P MAS NMR spectra of solid catalyst with high-power proton decoupling were performed at 161.9 MHz with BBO MAS probe head using 4 mm ZrO_2 rotors and 2.0 μs pulse and 2 s repetition time and 2048 scans, with samples spun at 8 KHz and referenced to 85% H_3PO_4.

3. Results and discussion

3.1. Characterization of catalysts structure

All six catalysts were characterized with FT-IR spectra. As shown in Fig. 1, an obvious feature of our catalysts is the lack of the peroxo band in position of $\nu(O\text{–}O) = 842$ [12], which is different from the catalysts of Venturello et al.

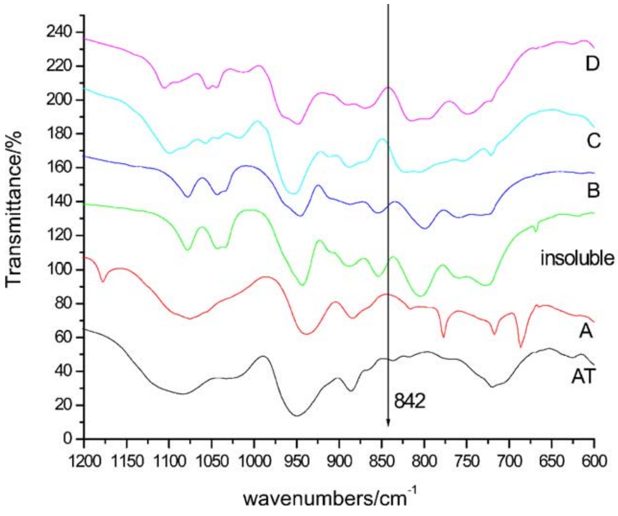


Fig. 1. FT-IR spectra of catalysts.

Table 1
Results of ICP characterization

Catalyst	P (wt.%)	W (wt.%)	Molar ratio of W/P
A	1.53	38.1	4.3:1
AT	1.91	37.0	3.3:1
B	0.83	37.1	7.5:1
Insoluble B	0.91	38.4	7.1:1
C	1.36	38.9	4.8:1
D	1.46	35.7	4.1:1

[2]. In cases of catalyst A and AT, the course of distillation at 60 °C abolished the O–O band. To catalyst C, the drying of catalyst under the infrared light broke up the O–O band. Similar to catalyst C, the peroxo band also does not exist in the catalyst B and catalyst D.

All six catalysts were characterized with ICP. As shown in Table 1, the W/P ratio of catalyst A, AT, C, D is between 3.3 and 4.8, but the catalyst B insoluble B is between 7.1 and 7.5.

All six catalysts were characterized with ^{31}P MAS NMR spectra. As shown in Figs. 2–7, all these catalysts are mixtures of several heteropolyphosphatotungstate species with different W/P ratio. For a reference, the spectrum of 12-tungsten phosphoric acid is also listed (Fig. 8). There is few result on ^{31}P MAS NMR spectra of heteropolyphosphatotungstates in the literature, but ^{31}P NMR spectra of heteropolyphosphatotungstates are studied quite detailedly. In the work of Salles et al. [7], the ^{31}P NMR band of PW_4, PW_3, PW_2 locate at $\delta = -3.5$, -1.6 and -0.5 ppm, respectively. Similarly, in the ^{31}P spectra of Hill et al. [6],

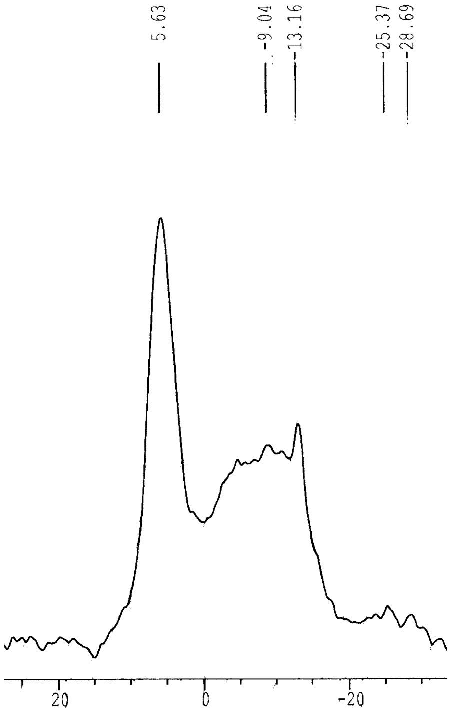


Fig. 2. ^{31}P MAS NMR spectrum of catalyst A.

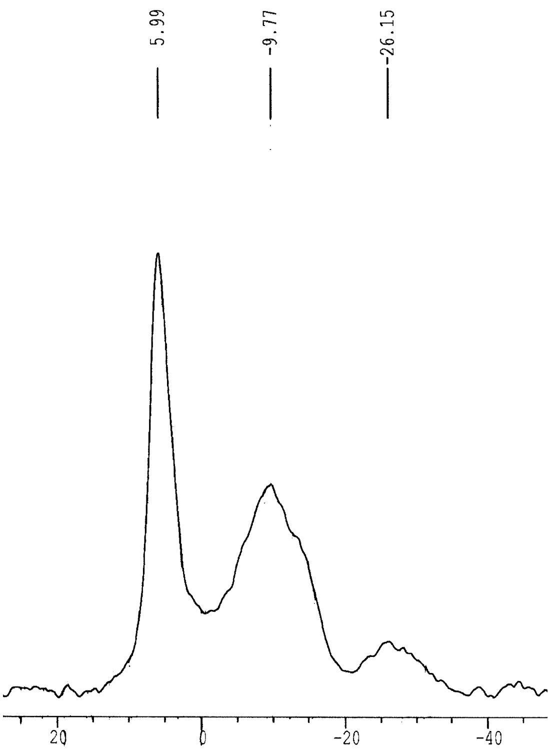


Fig. 3. ^{31}P MAS NMR spectrum of catalyst AT.

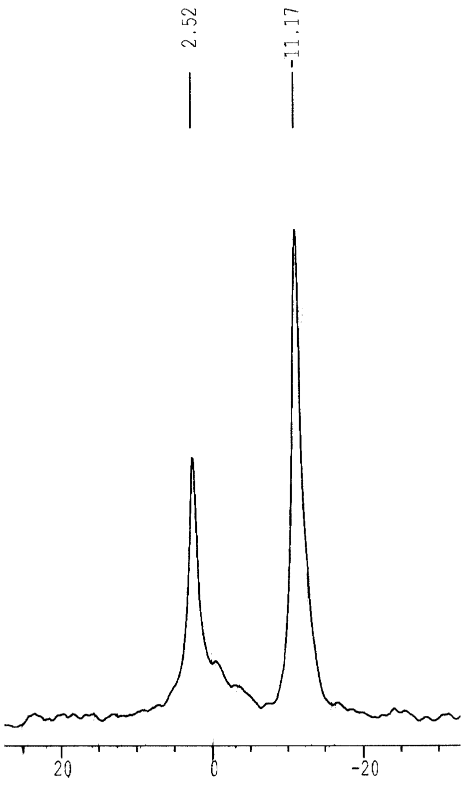


Fig. 4. ^{31}P MAS NMR spectrum of catalyst B.

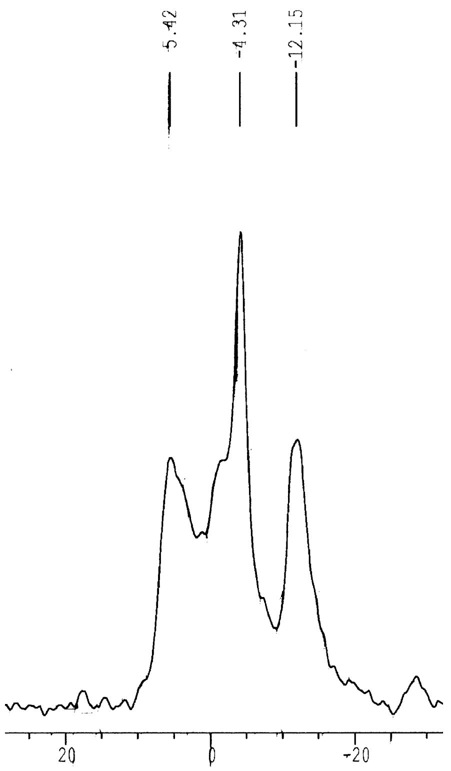


Fig. 5. ^{31}P MAS NMR spectrum of catalyst insoluble B.

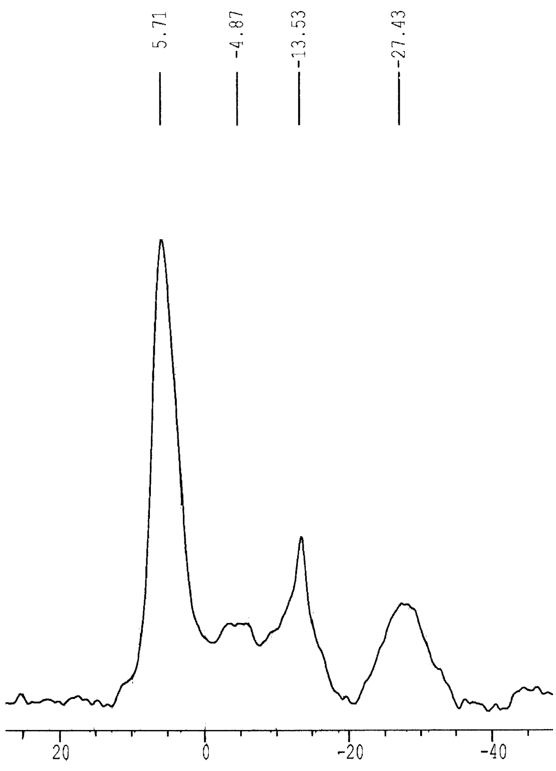


Fig. 7. ^{31}P MAS NMR spectrum of catalyst D.

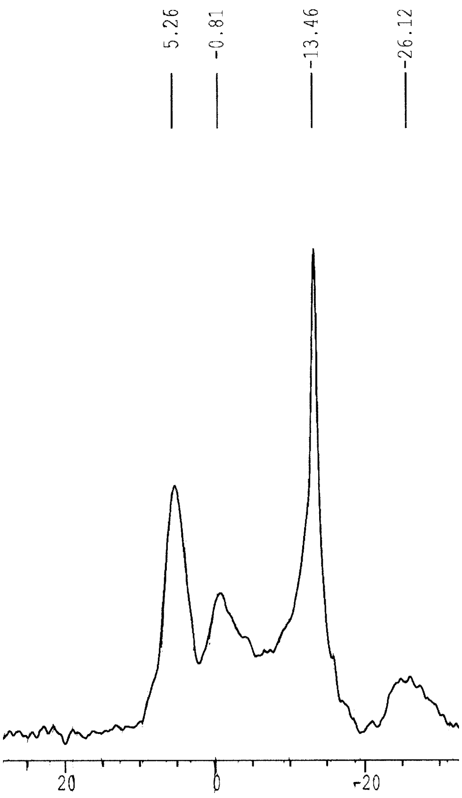


Fig. 6. ^{31}P MAS NMR spectrum of catalyst C.

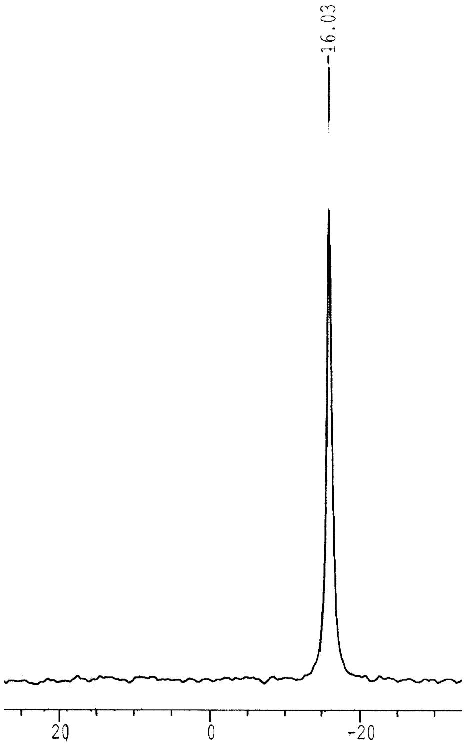


Fig. 8. ^{31}P MAS NMR spectrum of $H_3PW_{12}O_{40}$.

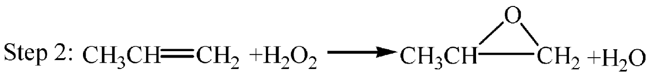
the band of PW_4 and PW_{12} is at $\delta = 0.6$ and -18.5 ppm, respectively. It proves sufficiently that the species with high *W*/*P* ratio locate at upfield compared with the species with low *W*/*P* ratio. In Fig. 7, the ^{31}P MAS NMR band of $H_3PW_{12}O_{40}$ is located at $\delta = -16$ ppm, a position near the ^{31}P NMR band of $H_3PW_{12}O_{40}$ solution [5]. So in the ^{31}P MAS NMR spectra, the bands located at low field compared with the band of $H_3PW_{12}O_{40}$ correspond to structure entities with low *W*/*P* ratio. In the spectra of catalyst A, AT, C, D the band at chemical shift ca. $\delta = 5$ ppm all appear obviously, which corresponds to a heteropolyphosphatotungstate structure entity with low *W*/*P* ratio. The catalyst A is obtained by distillating solvent in a water bath at 60 °C, not by gently evaporating solvent under reduced pressure at 40–50 °C as described by Venturello et al. [2], so it is inevitably that the peroxo bond O–O of catalyst A is broken up in the distillation step, leaving behind a mixture of many heteropolyphosphatotungstates with different P/W composition, whose overall composition are $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$. Because of the individual amounts of heteropolyphosphatotungstates are all small except the specie with ^{31}P MAS NMR band at ca. $\delta = 5$ ppm, there is no obvious band which can be attributed in the region behind the band at ca. $\delta = 5$ ppm in the ^{31}P MAS NMR spectrum of catalyst A. With the procedure of preparation essentially the same with the catalyst A except the cation is displaced by cetyltrimethyl ammonium chloride, the ^{31}P MAS NMR spectrum of catalyst AT is similar with that of catalyst A. In the spectra of Catalyst C and D, there are quite a few independent band except the band at ca. $\delta = 5$ ppm. In the spectrum of catalyst B, there are two distinct bands, but no the band at ca. $\delta = 5$ ppm is found. The *W*/*P* ratio of catalyst B is high, but after interaction with in situ H_2O_2, in the spectrum of insoluble B catalyst, the phosphatotungstate specie with the band at ca. $\delta = 5$ ppm emerges.

3.2. Propylene epoxidation reactivity of different heteropolyphosphatotungstate catalyst

In the course of experiment, the epoxidation of propylene in fact took place in two steps. In step 1,2-ethylanthrahydroquinone (EAHQ) was oxidized to 2-ethylanthraquinone (EAQ), accompanied by the production of H_2O_2.

$$\text{Step 1}: \quad \mathrm{EAHQ} + O_2 \rightarrow \mathrm{EAQ} + H_2O_2$$

In step 2, propylene was oxidized by in situ H_2O_2:



$$\text{Step 2: } CH_3CH{=}CH_2 + H_2O_2 \longrightarrow CH_3CH\overset{O}{\text{——}}CH_2 + H_2O$$

All the six catalysts were tested for the activity of step 2. In our previous work [13], the influence of reaction conditions had been studied very systematically. So in this paper, just optimized reaction conditions were selected. The results were listed in Table 2. Just as shown by soluble behavior test, catalyst A can dissolve completely into the reaction system. Under the reaction conditions, it can achieve a good yield (84.6%), and precipitate from the reaction solution while the H_2O_2 is used up, embodying the characteristic of “reaction controlled phase transfer”. The recovery efficiency of catalyst A is 96.8%. With the cation being replaced by cetyltrimethyl ammonium chloride, catalyst AT can also catalyze epoxidation of propylene with high reactivity too, with a yield close to catalyst A (84.3%). With different anions resulting from different preparation method compared with catalyst A and AT, the activity of catalyst C, D decrease slightly, but their propylene epoxide yield also surpass 80%. The *W*/*P* ratio of these four catalyst are all low, ca. 4 (see Table 1).However, the catalyst B with high *W*/*P* ratio (7.5) compared with the four catalysts mentioned above catalyze the reaction with a yield of only 53%.The poor reactivity of catalyst B results from two aspects. One aspect is the high *W*/*P* ratio, which determines the sum of PW_4 structure resulting from catalyst B is low, so its catalytic activity is accordingly bad [6]; the another aspect is its low solubility in situ H_2O_2 solution system. In the soluble behavior test, it can not dissolve completely at reaction temperature (65 °C). So its function as a homogeneous catalyst is relatively reduced. While catalyst B interacts with in situ H_2O_2 at room temperature, the catalyst “insoluble B” is obtained. The catalyst “insoluble B” is insoluble in reaction solution, but its ^{31}P MAS NMR spectra changes. The band at ca. $\delta = 5$ ppm appears (see Fig. 4). Correspondingly, the yield of propylene oxide increases (65.9%).

Table 2
Different catalysts for propylene epoxidation[a]

Catalyst	A	AT	C	D	B	Insoluble B
Yield (%)[b]	84.6	84.3	81.8	80.7	55.0	65.9

[a] 50 ml in situ H_2O_2 solution; H_2O_2/catalyst = 0.015 mol:0.1 g; propylene 2.65 g; 65 °C, 5 h.
[b] Yield based on H_2O_2.

From above results, the catalyst structure entity with ca. $\delta = 5$ ppm maybe is the precursor which can be the most efficiently converted to the “true active center”, $\{PO_4[WO(O_2)_2]_4\}^{3-}$ [6], which results from the interaction of a certain precursor with in situ H_2O_2, thus promotes epoxidation reaction of propylene. Furthermore, it seems to that the bigger the band at ca. $\delta = 5$ ppm occupy in the whole spectra, more efficiently the catalyst react. The further exploration of mechanism is under the way.

4. Conclusions

A series of heteropolyphosphatotungstate catalysts were prepared and characterized, their reactivity for propylene epoxidation was investigated. The results show, only heteropolyphosphatotungstates with low *W*/*P* ratio (ca. 4) have high reactivity towards propylene epoxidation, the band at ca. $\delta = 5$ ppm in ^{31}P MAS NMR spectra corresponds to a structure entity with low *W*/*P* ratio, which is the precursor which can be the most efficiently converted to the active center, $\{PO_4[WO(O_2)_2]_4\}^{3-}$.

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