



The oxidation of benzothiophene using the Keggin-type lacunary polytungstophosphate as catalysts in emulsion

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ABSTRACT

A series of emulsion catalysts were successfully synthesized with quarternary ammonium cations and heteropolyanions, and they were characterized by TG/DTA, FTIR, ³¹P MAS NMR and EPR. The emulsion catalyst with intact Keggin-structure, [C₁₈H₃₇N(CH₃)₃]₂[PW₁₂O₄₀] (PW₁₂), is inactive for benzothiophene (BT) oxidation with H₂O₂ as oxidant under atmospheric pressure at 30 °C. Moreover, the metal-substituted catalysts PW₁₁M (M=Ti, Mn, Fe, Co, Ni and Cu) show rather low activity with the conversion less than 15% for BT oxidation. Whereas, the catalyst with mono-lacunary Keggin-structures, [C₁₈H₃₇N(CH₃)₃]₅Na₂[PW₁₁O₃₉] (PW₁₁), could completely catalytic oxidize BT into the corresponding sulfone under the same conditions. After careful characterizations of the catalysts, it is found that only PW₁₁ catalyst could effectively transform into the active polyperoxometalates species in the presence of hydrogen peroxide in non-polar solvent.

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1. Introduction

SO_x produced from the burning of organic sulfur-containing compounds present in fuel oils not only can cause acid rain, air pollution, and harmfulness to human health, but also can poison irreversibly the three-way catalysts in the tail gas cleanup systems of engines. Therefore, ultra-deep desulfurization of fuel oils has been attracting researchers' attention and becomes one of the most challenging subjects for petroleum refining industry. Conventional hydrodesulfurization (HDS) is highly efficient in removing thiols, sulfides, and disulfides [1,2]. However, the capital investment and operating costs of HDS are both rather high due to more severe operating conditions to achieve the ultra-deep desulfurization [3–6]. As an alternative to the other desulfurization processes, oxidative desulfurization (ODS) [7–10] has stolen the limelight owing to its advantages like mild reaction conditions, being considered one of the most promising ultra-deep desulfurization processes. In this process, sulfur-containing compounds in fuels are oxidized with H₂O₂ using zeolitic titanasilicates [11–14], ionic liquids [15], or metal oxide catalysts [16,17]. Developing ultra-deep desulfurization catalysts with high activity has been one of the most challenging and important subjects.

Polyoxometalates (POMs) have been attracting much attention in the fields of acid and oxidation catalysis, because the acidic and redox properties of POMs can be designed and tuned at the molecular or atomic level [18–26]. POMs can be used as effective catalysts for benign oxidations of hydrocarbons with oxidants such as H₂O₂ or even O₂ [19–24]. For example, tungsten-based POMs have been demonstrated to be effective for the oxidation of olefins, alcohols, glycols, and phenols using H₂O₂ as oxidants [27–36].

In recent years, POMs, such as a quarternary ammonium polytungstophosphate catalyst assembled at the interface of the emulsion droplets, have been used for the oxidation of sulfur-containing compounds presented in fuel oils [37–40]. In our previous work [41,42], we reported two catalysts, [(C₁₈H₃₇)₂N(CH₃)₂]₃[PW₁₂O₄₀] and [C₁₈H₃₇N(CH₃)₃]₄[H₂NaPW₁₀O₃₆], assembled in an emulsion system. The former catalyst could selectively catalyze oxidation reaction of dibenzothiophene (DBT) and its derivatives into their corresponding sulfones under mild conditions with H₂O₂ as oxidant. The latter catalyst could catalytically oxidize benzothiophene (BT), which has much lower reactivity than DBT, to the corresponding sulfone. This work developed another quarternary ammonium polytungstophosphate [C₁₈H₃₇N(CH₃)₃]₅Na₂[PW₁₁O₃₉] with lacunary Keggin-structures, which could be used for oxidative desulfurization in emulsion system. It was found that the catalyst exhibit high catalytic activity toward the oxidation of BT under mild conditions; however, the catalytic activity decreased considerably when its lacunary sites were coordinated with the transition

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metal cations. It is implied that the mono-lacunary POMs could be propitious to the oxidation of BT.

2. Experimental

2.1. Preparation of catalysts

2.1.1. $[C_{18}H_{37}N(CH_3)_3]_5Na_2[PW_{11}O_{39}]$ (abbreviated as: PW_{11})

This compound was prepared consulting the synthesis of $[TBA]_4H_3[PW_{11}O_{39}]$ in the literature [43–45]. It is a direct synthesis process, which is starting from an aqueous solution of the required anion, to which was added a solution of octadecyltrimethylammonium chloride instead of TBA bromide. And the simple process is as following: sodium tungstate dehydrate (3.3 g), and disodium hydrogen phosphate (0.33 g) were dissolved in distilled water (80 mL), followed by adjusting pH to 4.8 with 1 M HNO_3 solution. The reaction mixture was then warmed up to 80 °C and a solution of octadecyltrimethylammonium chloride (1.6 g) dissolved in alcohol (20 mL) was added dropwise. A white precipitate was immediately formed. After continuous stirring for several minutes, the resulting mixture was filtered and dried at 60 °C in vacuum for 12 h to obtain PW_{11} .

The synthesis procedure of $PW_{11}M$ (M = Ti, Mn, Fe, Co, Ni and Cu) are quite similar as in the literature [43]. And here is the typical process: sodium tungstate dehydrate (3.3 g), disodium hydrogen phosphate (0.33 g) and cupric nitrate (0.22 g) were dissolved in distilled water (80 mL), followed by adjusting pH to 4.8 with 1 M HNO_3 solution. The reaction mixture was then warmed up to 80 °C and a solution of octadecyltrimethylammonium chloride (1.6 g) dissolved in alcohol (20 mL) was added dropwise. A kind of white precipitate was immediately formed. After continuous stirring for several minutes, the resulting mixture was filtered and dried at 60 °C in vacuum for 24 h to obtain $PW_{11}Cu$. Accordingly, $PW_{11}M$ (M = Ti, Mn, Fe, Co and Ni) samples were also synthesized following the above procedures by using the proper content of the corresponding nitrate or sulfate salts.

2.1.2. $[C_{18}H_{37}N(CH_3)_3]H_2[PW_{12}O_{40}]$ (abbreviated as: PW_{12})

A solution of octadecyltrimethylammonium chloride (0.35 g) in 20 mL of alcohol was added dropwise into 80 mL aqueous solution of $H_3PW_{12}O_{40}$ (2.9 g) under stirring at room temperature. A white precipitate was immediately formed. After continuously stirring for several minutes, the resulting mixture was filtered and dried at 60 °C in vacuum for 24 h to obtain PW_{12} .

2.2. Characterization of catalysts

X-ray fluorescence (XRF) was performed with a Panalytical Magix spectrometer to determine the Na/P molar ratio. Elemental analysis was performed on a PE2400 CHN elemental analyzer. Thermogravimetric and differential thermal analyses (TG–DTA) were performed using a Pyris Diamond TG/DTA thermal analyzer under a flowing air atmosphere. Transmission IR spectra were recorded from 32 scans with a resolution of 4 cm^{-1} using a KBr method by a Nicolet 470 Fourier transform infrared (FTIR) spectrometer. The high-power proton decoupling ^{31}P MAS NMR spectra were performed on a Bruker DRX 400 spectrometer operating at 161.8 MHz with a BBO MAS probe-head using 4-mm ZrO_2 rotors spun at 10 kHz. The recording parameters were set to be 2.0 μs pulse, 2 s repetition time, and 2048 scans. The ^{31}P chemical shift was normalized with 85% H_3PO_4 aqueous solution. X-band Electron Paramagnetic Resonance (EPR) spectra were recorded on a Bruker A-2000 X-band EPR spectrometer at 293 K. A microwave frequency of 9.40 GHz and a power of 20 mW were used. The spectra were calibrated with diphenylpicrylhydrazyl (DPPH: $g = 2.0036$).

2.3. Catalytic activity test

A typical procedure of the catalytic activity test is as follows: certain amount of BT was dissolved in a solution of decalin (25 mL) at 30 °C to quantify the sulfur content to be 1000 ppm. The catalysts (PW_{11} or metal-coordinated $PW_{11}M$) (0.015 mmol) and oxidant H_2O_2 (0.27 mL, 30 wt%) were added to the above BT solution simultaneously with a magnetic stirring at a speed of 1000 rpm. Immediate formation of turbid W/O emulsion was observed. To follow the reaction, the emulsion was sampled at a time interval of 1 h and stored in an icebox in order to quench the reaction. The catalyst in the sampled emulsion was separated from the emulsion phase by centrifugation. The content of BT in oil was determined by gas chromatography coupled with flame photometric detector (GC-FPD, Agilent 6890N equipped with a capillary column [PONA, 50 m \times 0.2 mm i.d. \times 0.5 μm]; FPD: Agilent H9261) under the following analytical conditions: injection port temperature, 280 °C; detector temperature, 250 °C; oven temperature, 280 °C; split ratio, 1/100; carrier gas, ultra-purity nitrogen with column flow of 0.8 mL/min; reagent gases, air and hydrogen with air flow of 100 mL/min and hydrogen flow of 85 mL/min; the injection volume of sample was 1 μL .

3. Results and discussion

3.1. Characterization of catalysts

In the curves of TG–DTA (Fig. 1), a distinct two-step weight loss process was observed for PW_{11} , with an inflexion at 443 °C. The first weight loss of 34.9% observed in the temperature range from 161 to 443 °C, was due to the decomposition of the alkyl chains of quaternary ammonium cations. The molar ratio of quaternary ammonium cations to heteropolyanions is 4.6:1. And the molar ratio of Na/P is determined to be 1.8:1.1 by XRF. According to the results of elemental analysis, the amount of C, H, and N are found to be 30.94%, 5.95%, and 1.52%, respectively. These results indicate that the molecular formula of the catalyst is mainly composed of $[C_{18}H_{37}N(CH_3)_3]_5Na_2[PW_{11}O_{39}]$, for which the amount of C, H, and N are calculated to be 29.41%, 5.37%, and 1.63%, respectively.

Fig. 2 shows the FTIR spectra of PW_{12} , PW_{11} , and $PW_{11}M$ (M = Ti, Mn, Fe, Co, Ni and Cu). The IR bands in the range of 700–1100 cm^{-1} are due to the contributions from the vibrations of P–O in the central PO_4 unit, W=O, and W–O–W [46–48]. The detailed vibrations assignments of PW_{12} , PW_{11} , and $PW_{11}Cu$ are summarized in Table 1. The spectra of PW_{12} exhibit the characteristic bands of $[PW_{12}O_{40}]^{3-}$ anion, and the distinct band at ca. 1080 cm^{-1} due

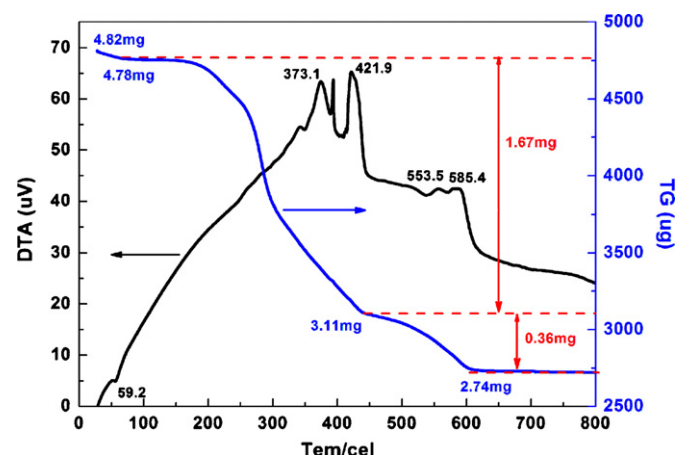


Fig. 1. TG–DTA curves of PW_{11} .

Table 1
IR bands assignments of POM and Cu coordinated POM catalysts.

Catalysts	Wavenumbers (cm ⁻¹)				
	$\nu_{\text{as}}(\text{P-O})$	$\nu_{\text{as}}(\text{W=O}_t)$	$\nu_{\text{as}}(\text{W-O}_c\text{-W})$	$\nu_{\text{as}}(\text{W-O}_e\text{-W})$	$\nu_{\text{as}}(\text{W-O-[Cu]})$
PW ₁₁	1078, 1045, 1035	945	891, 854	800	762, 727
PW ₁₁ Cu	1101, 1061	953	881	816, 797	748, 696
PW ₁₂	1080	978	897	808	–

ν_{as} : asymmetric stretching vibration; O_t: terminal oxygen; O_c: oxygen atoms connecting the corner-sharing WO₆ octahedra; O_e: oxygen atoms connecting the edge-sharing WO₆ octahedra.

to the vibration of the central PO₄ tetrahedron. As the symmetry decrease of the PO₄ tetrahedron in the structure of PW₁₁, this band is blue shifted and split into mainly two components, one with a peak maximum at 1078 cm⁻¹ and the other with a double band at 1045 and 1035 cm⁻¹, respectively. These FTIR observations are consistent with the reports in the literature [46–48], indicating that the structures of the primary heteropoly tungstophosphate anions remain intact after assembling with the quaternary ammonium cations (see Scheme 1). The IR spectra of PW₁₁Cu (Fig. 2) display one absorption band at 881 cm⁻¹, which belong to the vibration of W–O_c–W. This implies that the filling of the vacant in the octahedral lacunae by Cu cations restores the symmetry of the central tetrahedron to some extent owing to the interaction between Cu²⁺ and the available oxygen anions of the central PO₄ group. At the same time, all of the copper-coordinated catalysts and the lacunary catalyst PW₁₁ show that the band around about 800 cm⁻¹ is split into one broad band and two weak bands, which is an indication that the symmetry of the octahedron of WO₆ is distorted. Except a little blue shift in the range of 700–1000 cm⁻¹, the FTIR spectra of PW₁₁Cu are in well agreement with that of H₃PW₁₂O₄₀, which has a complete Keggin-structure. Similar phenomenon was also observed for the PW₁₁M sample treated by various other transition metals (M = Ti, Mn, Fe, Co, Ni, or Cu) (Fig. 2). Therefore, the FTIR spectroscopic study strongly implies that the metal ions should be coordinated with the lacunae of the Keggin-type structured samples.

The X-band EPR spectra (293 K) of PW₁₁ and PW₁₁Cu are shown in Fig. 3. The calculated *g* values are *g*_{||} = 2.408 and *g*_⊥ = 2.096 for PW₁₁Cu, respectively, which are in well agreement with the reports in the literature [49]. The special four weak hyperfine line splittings

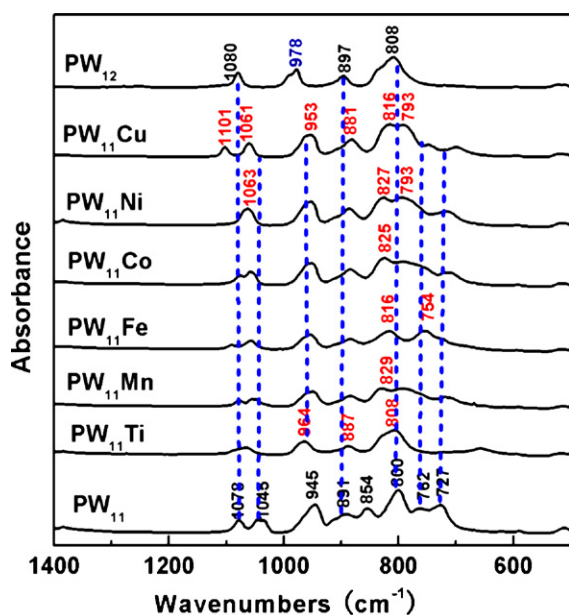
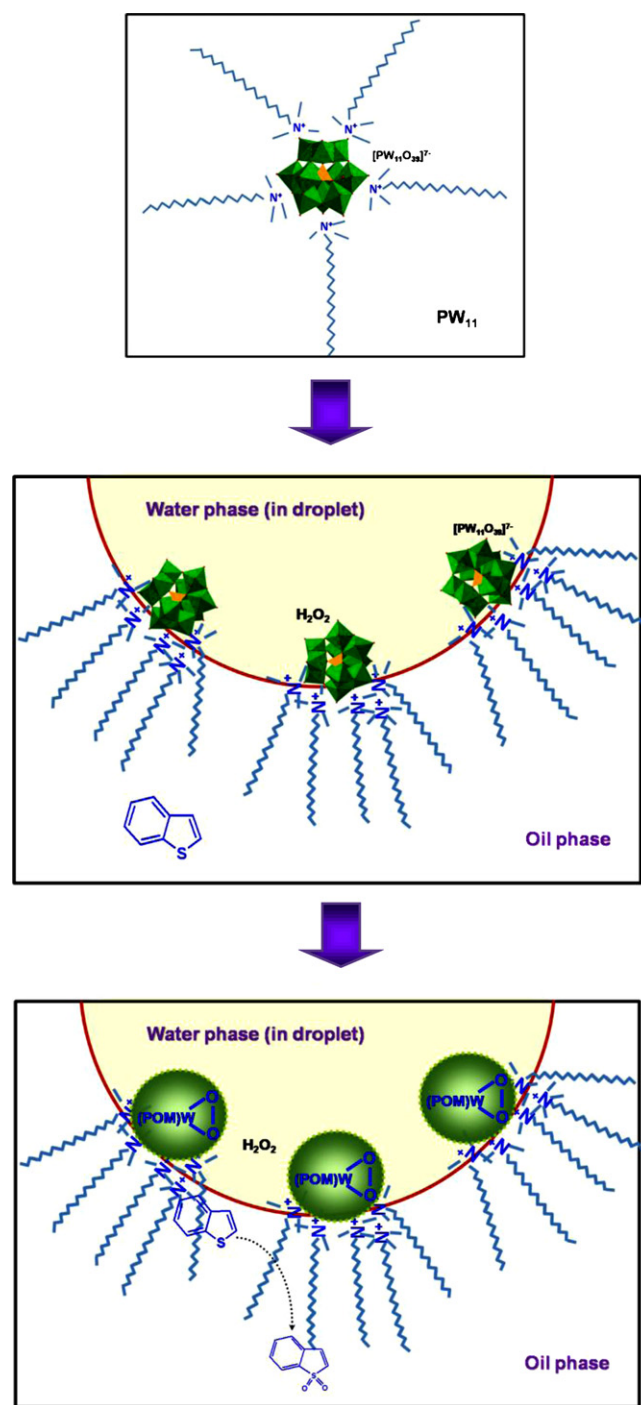


Fig. 2. FTIR spectra of PW₁₂, PW₁₁, and PW₁₁M (M = Ti, Mn, Fe, Co, Ni and Cu) for comparison.



Scheme 1. The amphiphilic catalyst PW₁₁ assembled at the interface of the emulsion droplet (O atom at the vertex of octahedron, W atom in the center of octahedron and P atom in the center of tetrahedron).

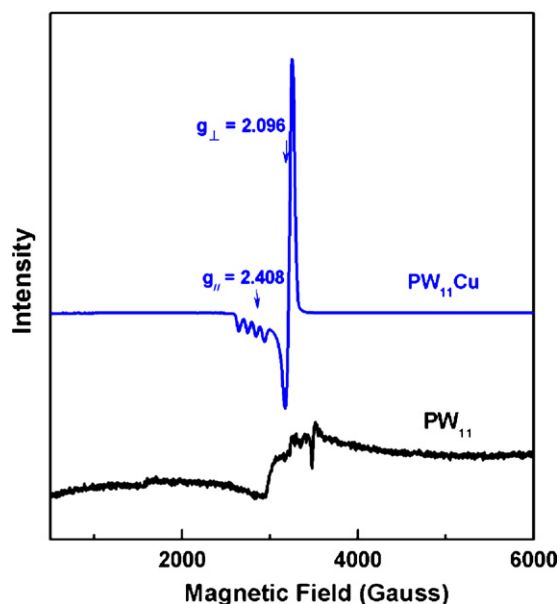


Fig. 3. X-band EPR spectra (293 K) of the catalysts: $PW_{11}Cu$ and PW_{11} .

with splitting constant of ca. 90 G in the EPR spectra of $PW_{11}Cu$ (Fig. 3) reveal that copper cations are located in a tetragonally distorted octahedral crystal field and surrounded by less than six ligands ($g_{\parallel} \neq g_{\perp}$) [50]. And the coordination form of copper is possibly a square-pyramidal belonging to five-coordinate copper(II) complexes ($g_{\parallel} > g_{\perp}$) [51].

The catalyst PW_{11} is also characterized by ^{31}P MAS NMR (Fig. 4) to confirm the structure. The peak at -10.2 ppm in Fig. 4 (in the middle) is due to the resonance of the central PO_4 unit of PW_{11} cluster, which is quite different from the chemical shift of PW_{12} at -15.1 ppm. As shown in Fig. 4 (at the bottom), it is interesting that no P species signal was found in the ^{31}P MAS NMR spectra of $PW_{11}Cu$, which may be resulted from the interaction of free copper cations to magnetic field. The further evidence is the ^{31}P MAS NMR spectrum of $PW_{11}Cu-EDTA$. After treatment by EDTA, two new signals appear in the ^{31}P MAS NMR spectrum of $PW_{11}Cu-EDTA$. As shown in Fig. 5, the peaks at -12.8 ppm and -15.6 ppm are originated from the central PO_4 unit of $PW_{11}Cu$ cluster and byproduct fragment of $[PW_{12}O_{40}]^{3-}$ [44,52], respectively. It should be also noted that the resonance of $PW_{11}Cu$ is shifted toward low fre-

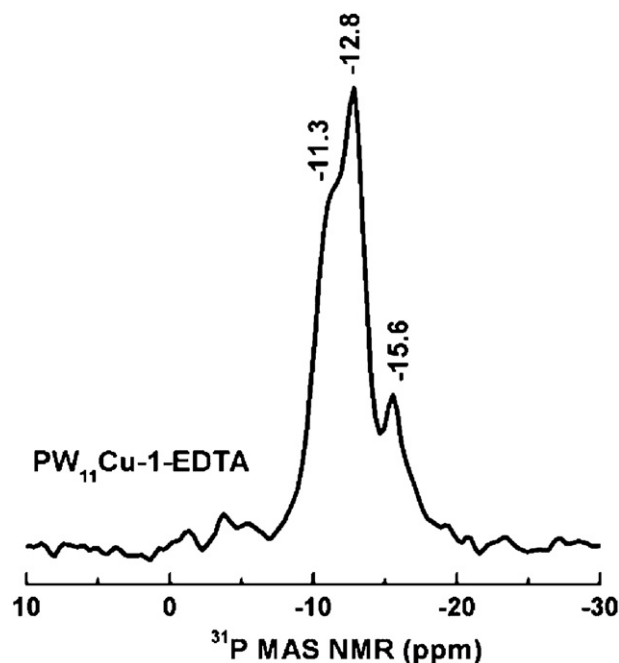


Fig. 5. ^{31}P MAS NMR spectra of the catalyst $PW_{11}Cu-EDTA$.

quency as compared with that of PW_{11} ($\delta = -10.2$ ppm), and near to that of the intact Keggin-type PW_{12} , which is much more stable than the lacunary Keggin-type PW_{11} . It is indicated that the incorporation of Cu possibly make the structure of PW_{11} to be more stable and rigid [53], which is even in agreement with the result of the IR blue shift. What is more, ^{31}P MAS NMR study also demonstrates that the structure of the PW_{11} cluster tend to be saturated after being coordinated by Cu cations, probably by the strong chemical interactions between copper and PW_{11} .

3.2. Catalytic reactions

The reaction activity data (Table 2) indicate the catalyst PW_{12} is inactive for the BT oxidation under the mild reaction conditions. The metal-substituted Keggin-type emulsion catalysts, $PW_{11}M$ ($M = Ti, Mn, Fe, Co, Ni$ and Cu), behave very much poor activity. However, under the same experimental conditions, the oxidation conversion of BT catalyzed by PW_{11} is 98%. The amphiphilic catalyst PW_{11} shows remarkably high activity toward BT oxidation in the emulsion catalytic systems. Peroxo-POMs have been proved to be the active intermediates in many reactions. The $\{PO_4[WO(O_2)_2]_4\}^{3-}$, one of the most active POMs for H_2O_2 -based oxidations, is the real active species in the Keggin-type $H_3PW_{12}O_{40}/H_2O_2$ system [30,31]. It was established that $[PW_{12}O_{40}]^{3-}$ and $[PW_{11}O_{39}]^{3-}$, which can rapidly convert into polyperoxometalate $\{PO_4[WO(O_2)_2]_4\}^{3-}$, are the effective species

Table 2

Conversions of BT oxidation on the various polyoxotungstate catalysts.

Catalyst	Conversion (%)
PW_{11}	98
PW_{12}	0
$PW_{11}Ti$	14
$PW_{11}Mn$	1
$PW_{11}Fe$	13
$PW_{11}Co$	3
$PW_{11}Ni$	1
$PW_{11}Cu$	3

Reaction conditions: $T = 30^\circ C$, BT (S: 1000 ppm) in decalin, $H_2O_2/BT = 3$, 1 h.

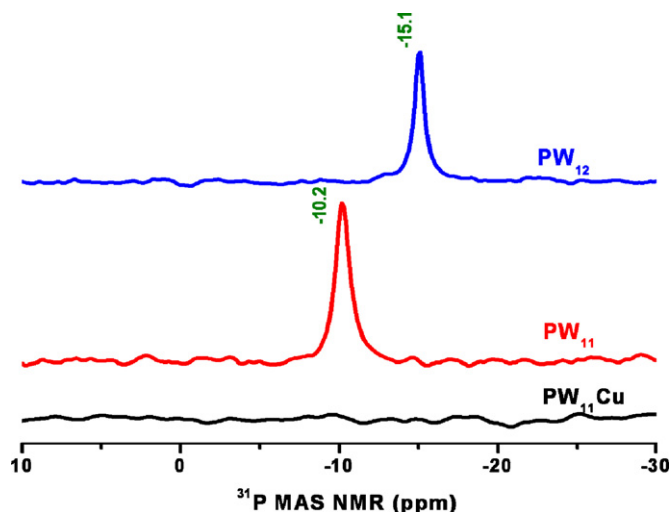


Fig. 4. ^{31}P MAS NMR spectra of the catalysts: PW_{12} , PW_{11} , and $PW_{11}Cu$.

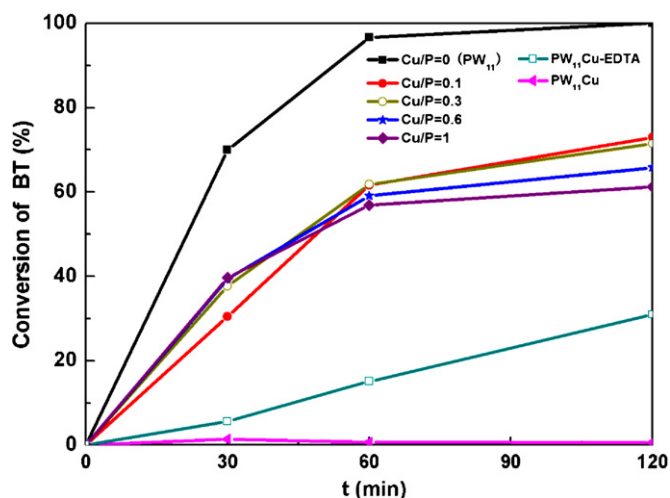


Fig. 6. Conversion of BT catalyzed by PW₁₁ + Cu (Cu/P = 0, 0.1, 0.3, 0.6, 1), PW₁₁Cu and PW₁₁Cu-EDTA, respectively. Reaction conditions: T = 30 °C, BT (S: 1000 ppm) in decalin, H₂O₂/BT = 3.

for the epoxidation of the terminal alkenes [31]. In addition, a peroxotungstate complex has been shown to be the active oxidizing species. Rui Zhang's group [54] has reported that a tungsten peroxy complex rather than a high valent transition-metal oxo species operates as the key intermediate in the sandwich-type POM-catalyzed epoxidations of chiral allylic alcohols. The similar phenomenon may be in the present reaction system with PW₁₁ as catalyst (see more evidences and results in the corresponding Supplementary material). The amphiphilic catalysts PW₁₂ and PW₁₁ are assembled at the interface of the emulsion droplets (as shown in Scheme 1). Furthermore, decalin is non-polar solvent, of which the character is quite different from polar solvent used in the reported oxidation system [31], and the amphiphilic catalyst PW₁₁ could much more rapidly form polyperoxometalate than that PW₁₂ do in the H₂O₂-based oxidation system. On the other hand, it is observed that the catalytic activity of PW₁₁ can be largely blocked by the coordination of transition metals (Ti, Mn, Fe, Co, Ni and Cu) (see the results in Table 2). The reason is that PW₁₁M (M = Ti, Mn, Fe, Co, Ni and Cu) with the intact Keggin-structure could not effectively transform into the active polyperoxometalate in the presence of hydrogen peroxide. Furthermore, the reduction of the catalytic activity may be related with the coordination capability of the transition metals. Among these transition metals, coordination of manganese or nickel results in the lowest catalytic activity due to the stronger interactions between the metals (manganese or nickel) and the lacunae of PW₁₁.

In order to investigate the effect of the free copper cation on the catalytic activity of PW₁₁ for BT oxidation, a certain amount of copper salt was added into the reaction mixture. A visible decrease of BT conversion is observed even if the Cu/P molar ratio was only 0.1, as shown in Fig. 6. The conversion of BT was about 60% in 2 h when Cu/P molar ratio was 1. However, the conversion of BT catalyzed by PW₁₁Cu was close to zero under the same reaction conditions. In order to investigate the interaction between copper and heteropolyanions, PW₁₁Cu was treated with 20-fold stoichiometry of ethylene diamine tetraacetic acid (EDTA) as coordination reagent, and the obtained sample is described as PW₁₁Cu-EDTA. The IR spectra of the structure of PW₁₁Cu were nearly remained after being treated by EDTA (Fig. 7). However, the catalytic activity of PW₁₁Cu-EDTA was significantly improved compared with that of PW₁₁Cu (Fig. 6). Conversion of BT catalyzed by PW₁₁Cu-EDTA could reach up to 94% in 9 h. When the catalyst PW₁₁ was mixed with copper nitrate (abbreviated as: PW₁₁ + Cu), though the initial reaction

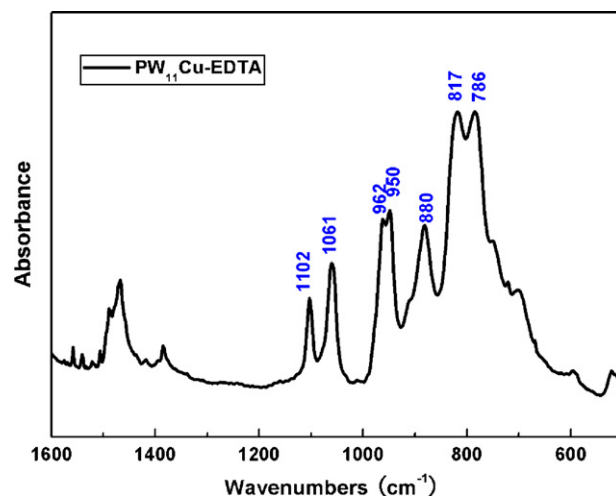


Fig. 7. FTIR spectra of PW₁₁Cu-EDTA.

rate was quite high, it became quite slow after 2 h. The concentration of hydrogen peroxide solution is determined by cerous sulfate titration method, and the results are listed in Table 3. The decomposition conversion of H₂O₂ at 30 °C in 1 h is only 8.1% in the presence of PW₁₁, but is 50.0% and 60.7% in the presence of PW₁₁Cu and PW₁₁ + Cu, respectively. Treatment of PW₁₁Cu with EDTA can significantly inhibit the decomposition conversion of H₂O₂, as evidenced by the only 1.5% H₂O₂ decomposition in 1 h in the presence of PW₁₁Cu-EDTA. In the meantime, the conversion of BT in 1 h is 15.1% by PW₁₁Cu-EDTA, which is much higher than 0.7% by PW₁₁Cu. These results indicate that a proportion of copper cations weakly interacts with the catalysts and can be easily removed from the PW₁₁ catalyst by the treatment with EDTA. Moreover, these copper cations could accelerate the decomposition of hydrogen peroxide, leading to the insufficient oxidant for BT oxidation to proceed. However, the catalytic activity of PW₁₁Cu-EDTA was still much lower than that of PW₁₁ under the same experimental conditions, indicating that treatment with EDTA can only remove copper cations weakly bounded with PW₁₁, but those copper cations, which have strong interactions with PW₁₁, remain therein. Therefore, the low catalytic activity is due to not only the side reaction of H₂O₂ decomposition but also the transformation of the intact Keggin-structure catalysts into active polyperoxometalate being blocked by the metal cations (M = Ti, Mn, Fe, Co, Ni and Cu) in the presence of hydrogen peroxide. This made us draw a conclusion that the metals coordinating with the lacunary heteropolyanions lead the catalyst lose activity for the oxidation of sulfur-containing compounds, such as BT.

Table 3
H₂O₂ decomposition on PW₁₁ catalysts in the presence of Cu cation.

Catalyst	Final concentration of H ₂ O ₂ ^a (wt%)	H ₂ O ₂ decomposition conversion ^b (%)
PW ₁₁	24.8	8.1
PW ₁₁ + Cu ^c	10.6	60.7
PW ₁₁ Cu	13.5	50.0
PW ₁₁ Cu-EDTA ^d	26.6	1.5

Reaction conditions: T = 30 °C, decalin (25 mL), the initial concentration of H₂O₂ (0.306 mL) is 27 wt%.

^a The concentration of H₂O₂ after 1 h.

^b H₂O₂ decomposition conversion after 1 h.

^c Cu/P (mol/mol) = 1.

^d PW₁₁Cu after treating with EDTA.

4. Conclusion

Under mild conditions, mono-lacunary polyoxotungstates catalyst PW₁₁ shows high catalytic activity on the oxidation of BT in emulsion. Once the lacunae are coordinated by the transition metal cations, the catalysts will lose the catalytic activity. It is proved that the well performance of these catalysts could be due to the mono-lacunary Keggin-structures of the tungstophosphoric compounds, which could rapidly transform into the active polyperoxometalate in the presence of hydrogen peroxide. And it is important for ultra-deep desulfurization of fuel oil to further investigate the reaction mechanism between lacunary polyoxotungstates and sulfur-containing compounds.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.08.021.

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