Short Communication

Efficient oxidation of sulfides catalyzed by a temperature-responsive phase transfer catalyst [(C$_{18}$H$_{37}$)$_2$(CH$_3$)$_2$N]$_7$ PW$_{11}$O$_{39}$ with hydrogen peroxide

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ABSTRACT

A temperature-responsive phase transfer catalyst [(C$_{18}$H$_{37}$)$_2$(CH$_3$)$_2$N]$_7$PW$_{11}$O$_{39}$, could act as an efficient catalyst for selective oxidation of sulfides with 30% aqueous H$_2$O$_2$. Various kinds of sulfides were successfully oxidized to their corresponding sulfones with over 96% yields in a relatively short time and mild conditions. During reaction at 333 K, the catalyst dissolved completely and the oxidation was conducted homogeneously. Before and after reaction, the catalyst was insoluble with cooling, so it is easily recovered and reused. The catalyst was characterized by elemental analysis, FT-IR and ^{31}P NMR.

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1. Introduction

The exploring of the highly efficient catalytic systems for the oxidation of sulfides to sulfoxides and sulfones is of great importance [1,2], because they are important intermediates in organic synthesis and biologically active molecules [3–5]. Additionally, oxidative desulfurization to yield sulfoxides or sulfones, as the better alternative way compared with traditional hydrodesulfurization process, has aroused attention because of high desulfurization efficiency [6]. H$_2$O$_2$, commonly considered as the "green oxidant", was widely employed as terminal oxidant because of its natural advantage such as high atomic efficiency and H$_2$O as sole by product, so it is undoubtedly to be an ideal option in sulfides oxidation catalysis [7–9].

Many catalytic systems with H$_2$O$_2$ have been implied on sulfides oxidation in the past decades. For example, using ionic liquids [10,11], mesoporous silica–titania [12,13], LDHs [14,15], polymer-immobilized peroxotungsten catalyst [16], metal catalysts including Se, Mn, Re [17–19], etc. Polyoxometalates, having sophisticated structure with the characteristic of tunability, are widely used in catalysis with the development of POMs chemistry owing to their inherent redox and acidic properties [20–22]. In the past decades, using POMs on sulfides oxidation reactions have been reported widely in homogeneous catalysis, emulsion catalysis and heterogeneous catalysis [5,8,22–28]. For example, Li et al. synthesized polytungstophosphate anions [23]

and Anderson-type [IMo$_6$O$_{24}$]$^{5-}$ [24] combined with different quaternary ammonium cations assembled in emulsions to oxidize some dibenzothiophene (DBT) derivatives. Mizuno reported that [TBA]$_4$ [γ-SiW$_{10}$O$_{34}$(H$_2$O)$_2$] [5] and [γ-PW$_{10}$O$_{38}$V$_2$(μ-OH)$_2$]$^{3-}$ [22] homogeneously catalyze oxidation of various sulfides. Polyoxometalate-based ionic liquids [25,26] and H$_3$PW$_{12}$O$_{40}$ supported nanoparticles catalysts were also reported on DBT oxidation [27].

Herein, we endeavored to synthesize a novel temperature-responsive phase transfer catalyst [(C$_{18}$H$_{37}$)$_2$(CH$_3$)$_2$N]$_7$PW$_{11}$O$_{39}$, and catalyze oxidation of a series of sulfides including thioether and thiophene derivatives. This catalyst is composed of bulky organic cation and keggin-type lacunary [PW$_{11}$O$_{39}$]$^{7-}$ anion, which possess the characteristic of temperature sensitivity in the mixture of aqueous H$_2$O$_2$/1,4-dioxane. Both the advantage of high efficiency in homogeneous catalysis and catalyst recycling in heterogeneous catalysis are combined in this system [29,30]. The catalyst was insoluble in the system at room temperature, but dissolved with the elevation of reaction temperature. After the reaction finished with cooling, the catalyst precipitated gradually from the system itself. The catalyst effectively catalyzed the oxidation and could be easily recovered and reused.

2. Experimental

2.1. Preparation of catalyst

All reagents used in this work are commercially available and were used as received without further purification unless otherwise

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Table 1
Oxidation of benzothiophene under different solvents with [(C_18H_37)_2(CH_3)_2N]_7 PW_11O_39.[a]

Entry	Solvent	Conversion (mol%)	Selectivity (mol%)
1	1,2-dichloroethane	97	99
2	acetonitrile	67	99
3	acetone	26	99
4	water	56	87
5	ethanol	62	99
6	toluene	41	99
7	ethyl acetate	74	99
8	1,4-dioxane	99	99

[a] Reaction conditions: 333 K, 0.5 h, substrate 1 mmol, H_2O_2 2.5 mmol, 2 ml solvent. Conversion and selectivity were determined by GC analysis and bromobenzene was used as internal standard.

stated. First, 30 g of $Na_2WO_4 \cdot 2H_2O$ was dissolved in 37 ml of distilled water with stirring. Then 0.75 ml of 85% H_3PO_4, followed by 5.5 ml of acetic acid, was added to the stirring solution. After a while the solution became cloudy and gradually a heavy white precipitate formed. The solid was collected and first dried under vacuum for 24 h, then it was left in air for 24 h, finally, it was dried at 140 °C for about 1.5 h to get the solid of Δ-$Na_8H[PW_9O_{34}] \cdot 19H_2O$ [31]. Then, 0.56 g of Δ-$Na_8H[PW_9O_{34}] \cdot 19H_2O$ was dissolved in 55 ml of water. To this solution, 0.9 g of dioctadecyl dimethyl ammonium chloride dissolved in 10 ml of tert-butanol was added slowly. The mixture was stirred vigorously for 4.5 h at 40 °C. A white solid was filtered off and then washed with an excess amount of water, then dried in vacuum [29]. The yield was 81%. IR spectrum (KBr, cm^{-1}): 1079, 1043, 1033, 944, 896, 854, 803, 760, 721, 590, 547, 508, 433, 410. ^{31}P NMR: − 9.7 ppm. Calcd for [(C_18H_37)_2(CH_3)_2N][PW_11O_39]: C, 48.90; H, 8.58; N, 1.50; P, 0.47; W, 30.98. Found: C, 47.93; H, 8.54; N, 1.44; P, 0.44; W, 30.21.

2.2. Characterization techniques

Infrared spectra were recorded on a Bruker VERTEX 70v FT-IR spectrometer. The catalysts were measured using 2–4% (w/w) KBr pellets prepared by manual grinding. ^{31}P NMR and ^{1}H NMR spectra were recorded on a Bruker AVANCE III 400 M NMR using $CDCl_3$ as the solvent and Me_4Si as the internal standard. GC analyses were performed on a Shimadzu GC-9AM gas chromatogram with a flame ionization

Table 2
Oxidation of sulfur containing compounds with [(C_18H_37)_2(CH_3)_2N]_7 PW_11O_39.[a]

Entry	Substrate	Product	Conversion (mol%)	Selectivity (mol%)
1			97	99
2			99	99
3			99	99
4			99	99
5			98	99
6			99	99
7			97	99
8			99	99
9			99	99
10[b]			5	99
11[c]			no	–

[a] Reaction condition: 333 K, 0.5 h, substrate 1 mmol, H_2O_2 2.5 mmol, 8 μmol catalyst, 2 ml 1,4-dioxane as solvent. [b] without catalyst. [c] without H_2O_2. Conversions and selectivity were determined by GC analysis. Products were identified by ^{1}H NMR.
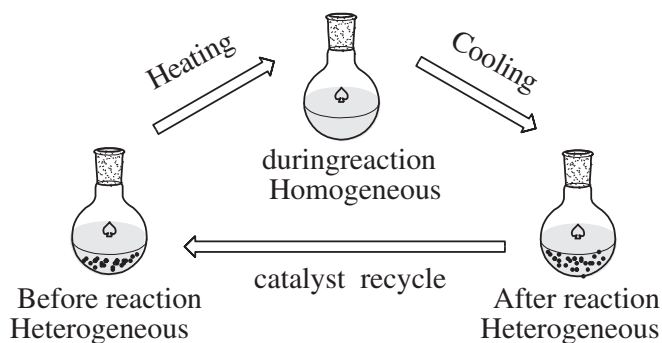
Scheme 1. Representation of the temperature-responsive phase transfer catalytic process.

detector equipped with SE-54 capillary (30 m × 0.32 mm × 0.25 μm). Chemical elemental analysis of the catalyst was done on an ICP-atomic emission spectrometer (IRIS ER/S).

2.3. Catalytic reaction

Catalyst (8 μmol), 1,4-dioxane (2 ml), substrate (1 mmol), and H_2O_2 (2.5 mmol, 30% aq.) were charged in the reaction flask. The reaction was carried out at 333 K for 0.5 h. After reaction, with the dropping of temperature, the catalyst gradually precipitated from solution. It was separated by centrifugation and washed with Et_2O, then dried under vacuum and used for the next oxidation cycle. The filtrate was analyzed by GC using bromobenzene as internal standard. The organic products were obtained by vacuum rotary evaporator, and identified by ^{1}H NMR. (See supporting information).

3. Results and discussion

It's known that the reactivity of common sulfur compounds in oxidation is commonly in the following order: benzothiophene <dibenzothiophene<diphenylsulfide<methylphenylsulfide [15]. Because this oxidation reaction was generally considered to proceed via an electrophilic addition reaction of oxygen atoms, so the sulfides with higher electron density on the sulfur atom should react easier [23]. Here we chose the relatively inert sulfide of benzothiophene (BT), as the model substrate to investigate. Excess oxidant H_2O_2 was used to afford it's unavoidably decomposing under the heating temperature (substrate: H_2O_2 = 1: 2.5).

Firstly, the catalyst of [(C_18H_37)_2(CH_3)_2N]_7PW_11O_39 was tested in different solvents (Table 1). BT was almost completely oxidized in 1,2-dichloroethane (entry 1), but this solvent was carcinogenic and could dissolve this catalyst at room temperature which hindered
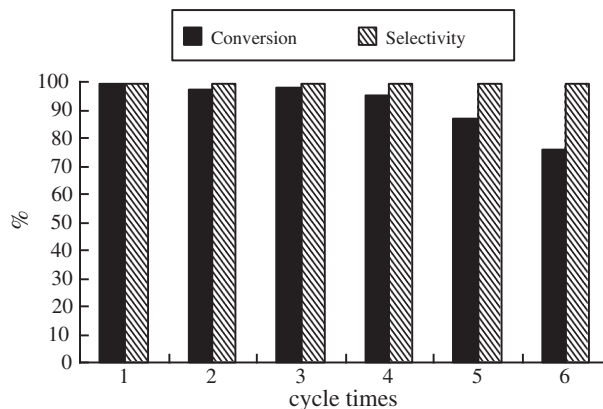

Fig. 1. Catalyst recycles for oxidation of benzothiophene. Reaction conditions were the same with those in Table 2.