



Short Communication

The epoxidation of olefins catalyzed by a new heterogeneous polyoxometalate-based catalyst with hydrogen peroxide

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ABSTRACT

Inorganic–organic hybrid material was formed by $[PW_{11}O_{39}]^{7-}$ and benzene-1,3,5-[tris(phenyl-4-carboxylic acid)] tris(2-trimethyl-ammonium ethyl) ester. This hybrid material behaved as a very effective and selective heterogeneous catalyst for the epoxidation of olefins with hydrogen peroxide as an oxidant. This heterogeneous catalyst could be easily recovered and reused after reaction without loss of activity.

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1. Introduction

The oxidation of olefins is very attractive from the viewpoint of industrial production, because epoxides are one of the most important precursors of various fine chemicals and a catalytic olefin epoxidation system that uses hydrogen peroxide as a terminal oxidant offers advantages [1–6]. Polyoxometalates (POMs) are molecular metal–oxygen clusters with discrete structures. The chemistry of POMs has attracted much attention, and the versatility and accessibility of POMs have led to many applications in various areas [7]. A great number of results have been reported on olefin epoxidation with POMs as catalysts and hydrogen peroxide as an oxidant. For example, Venturello's [5,8] and Ishii's [6,9,10] $[PO_4[WO(O_2)_2]_4]^{3-}$ and $[PW_{12}O_{40}]^{3-}$, Mizuno's [11] $[\gamma-SiW_{10}O_{34}]^{4-}$ and Neumann's [12] $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ as homogeneous catalysts and Ding's [13,14] $[PW_4O_{32}]^{3-}$ and Xi's [15–17] $[PW_4O_{16}]^{3-}$ as phase-controlled catalysts were shown to catalyze the olefin epoxidation with hydrogen peroxide and good results have been obtained.

Efficient separation of POMs catalysts and their reuse become the most important single issue that should be emphasized for industrial application. The catalysts can be easily separated from reaction solution by using a method of solid–liquid separation. For that reason, synthesis of new supports and design of new pathways for immobilization of homogeneous catalysts based on POMs are necessary [18–22]. Thus, various high-surface-area supports, such as multi-wall carbon nanotubes [23], ion-exchange resin [24], mesoporous molecular sieves [25], and silica [26], have been used for POMs immobilization.

Herein, we report on the synthesis of a tripodal organic triammonium cation, benzene-1,3,5-[tris(phenyl-4-carboxylic acid)] tris(2-trimethyl-ammonium ethyl) ester (BTE), and its utilization as building blocks together with $[PW_{11}O_{39}]^{7-}$, to yield a heterogeneous catalyst (BTE- $PW_{11}O_{39}$). This organic-POMs material is widely insoluble in many kinds of solvents. The obtained material has been characterized by FT-IR and ^{31}P MAS NMR. For the first time, we use this heterogeneous catalyst for olefin epoxidation, and its activity of olefin epoxidation using hydrogen peroxide as an oxidant has been studied.

2. Experimental

2.1. Preparation of BTE- $PW_{11}O_{39}$

The experiment detail of synthesis procedure of BTE- $PW_{11}O_{39}$ was described in supporting information section. Briefly, BTE- $PW_{11}O_{39}$ was synthesized by following route (see supporting information Scheme 1): 4-bromacetophenone self-condensed to yield 1,3,5-tris(4-bromophenyl)-benzene (1) according to a literature procedure [27]. 1,3,5-tris(4-bromophenyl)-benzene was reacted with *n*-BuLi to produce a light-green precipitation which followed by carboxylation with carbon dioxide yielded 1,3,5-tris(4-carboxyphenyl)benzene (2) [28]. After preparation of the acyl chloride derivative, esterification with *N,N*-dimethylaminoethanol yielded the benzene-1,3,5-[tris(phenyl-4-carboxylic acid)] tris-(2-di-methylamioethyl) ester (3), which was quaternized by methylation with an excess of dimethyl sulfate to yield the methyl sulfate salt (BTE) [29].

1 equiv of $[n-Bu_4N]_7[PW_{11}O_{39}]$ dissolved in DMSO with 3 equiv of BTE, also dissolved in DMSO, yielded white, amorphous solids (BTE-

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PW₁₁O₃₉) almost immediately upon mixing the solutions. The final catalyst was obtained by filtration or centrifugation.

2.2. Catalytic reaction

The catalytic reaction was performed in a 5 mL round-bottomed flask equipped with an oil bath, a magnetic stirring bar and a reflux condenser. In a typical experiment, hydrogen peroxide (30%) (0.5 mmol), acetonitrile (0.75 mL), cyclohexene (2.5 mmol) and catalyst (3.6 μmol) were added in the flask. The reaction was performed at 60 °C and was monitored by GC analysis. After 1.5 hours, conversion of the substrate was measured by GC with the internal standard method. Assignments of products were made by comparison with authentic samples. Selected products were also analyzed by GC/MS (Finnigan Trace DSQ). The catalyst was recovered by centrifugation after the reaction, washed with DMSO and diethyl ether.

3. Results and discussion

3.1. Catalyst characterization

The hybrid organic POM compound, BTE-PW₁₁O₃₉, was characterized by IR spectra (Fig. 1(a), (b), (c)), which showed via the expected absorption maxima that both the POM anion moiety [PW₁₁O₃₉]⁷⁻ (1109, 1049, 954, 893, 811, 768, and 517 cm⁻¹) [30] and BTE ($\nu_{\text{C-H(Ar)}}$ 3037, $\nu_{\text{C-H(Alk)}}$ 2952, $\nu_{\text{C=O}}$ 1716, $\nu_{\text{C=C}}$ 1627, 1605 cm⁻¹) were retained in the hybrid material. Our data suggested that there were no apparent changes in structure, after the POM anion being immobilized in the BTE.

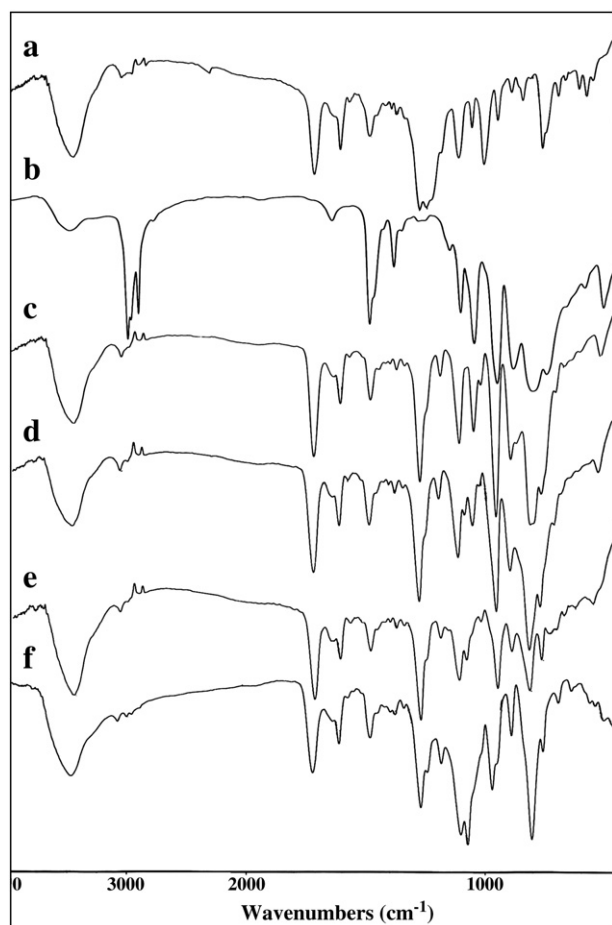


Fig. 1. FT-IR spectra of (a) BTE; (b) [n-Bu₄N]₇[PW₁₁O₃₉]; (c) the fresh catalyst of BTE-PW₁₁O₃₉; (d) the used BTE-PW₁₁O₃₉ for cycle 1; (e) the used BTE-PW₁₁O₃₉ for cycle 10; (f) BTE-PW₁₁O₃₉ treated with hydrogen peroxide.

3.2. The epoxidation of olefins

The organic–inorganic hybrid material, BTE-PW₁₁O₃₉, as a new heterogeneous catalyst was applied to olefin epoxidation with hydrogen peroxide. Several experiments were performed to test the catalytic activity of BTE-PW₁₁O₃₉. In reactions performed by the procedure as described in the experimental section, epoxidation of olefins to corresponding epoxides was very effective.

The solvent effect of epoxidation of cyclohexene was studied with different solvents (Table 1). The epoxidation with hydrogen peroxide using BTE-PW₁₁O₃₉ as catalyst was carried out at the same temperature (60 °C) in different kinds of solvents. During the reaction, the catalyst of BTE-PW₁₁O₃₉, acted as a heterogeneous catalyst, was insoluble in these solvents. BTE-PW₁₁O₃₉ could be well dispersed to all these solvents except toluene. However, high yield was achieved only in the system of using acetonitrile as solvent. The activity of epoxidation was middle to poor in other solvents such as chloroform, dioxane etc.

The catalytic activity of BTE-PW₁₁O₃₉ was investigated for the epoxidation of several types of olefins (such as cyclic olefins, terminal olefins and allylic alcohols) with hydrogen peroxide as the oxygen donor in acetonitrile both at 60 °C and 30 °C. The results in Table 2 for the epoxidation of olefins show that BTE-PW₁₁O₃₉ effectively catalyzes the olefin epoxidation in middle to good conversion and selectivity. High conversions and selectivities for the epoxidation of cyclohexene, 1-methyl cyclohexene, and cyclooctene were observed under our reaction conditions (hydrogen peroxide/olefin/catalyst = 1 mol: 5 mol: 0.0072 mol) at 60 °C (entries 1, 3 and 5). Styrene was converted to styrene oxide and benzaldehyde which was formed by C=C bond cleavage (entry 7). For allyl alcohol, no acrylaldehyde was observed and the selectivity to oxiran-2-ylmethanol was good (entry 9). It was regretful that the conversion of 1-octene was not quite good (conversion = 56%), even if the reaction time was prolonged (entry 11). At 30 °C, conversions and selectivities for cyclohexene, 1-methyl cyclohexene, cyclooctene and allyl alcohol were similar to the reaction being performed at 60 °C, when the reaction time was prolonged (entries 2, 4, 6 and 10). For styrene and 1-octene, the catalyst was not efficient under the low temperature (30 °C) condition (entry 8, 12).

The activity of BTE-PW₁₁O₃₉ was tested (entries 13–14) at low catalyst loading. Hundreds of catalytic TOF were obtained. TON and TOF for cyclohexene were about 5400 and 450 h⁻¹, respectively. For cyclooctene were about 7300 and 730 h⁻¹. The high TOF indicated that BTE-PW₁₁O₃₉ was quite effective for the epoxidation of olefins.

In the use of hydrogen peroxide as an environmentally benign, terminal oxidant, we had found, that [PW₁₁O₃₉]⁷⁻ was a real active composition for the epoxidation of a model olefin, cyclohexene, to selectively yield the corresponding cyclohexene oxide. Using BTE only

Table 1
Epoxidation of cyclohexene on catalyst BTE-PW₁₁O₃₉ under different solvent.

Entry	Solvent	Selectivity (mol%)	Conversion (mol%)	TON
1	Acetonitrile	>99	93	129
2	Ethyl acetate	>99	51	71
3	Acetone	>99	63	87
4	Water	–	0	0
5	Tetrahydrofuran	>99	40	55
6	Chloroform	>99	17	24
7	Toluene	>99	3	4
8	Dioxane	>99	16	22

Reaction conditions: 2.5 mmol alkene; 0.5 mmol hydrogen peroxide; 3.6 μmol catalyst; 0.75 mL solvent; reaction temperature: 60 °C, 1.5 h, conversion (%) = epoxide (mol)/hydrogen peroxide (mol). Selectivity (%) = epoxide (mol)/all products (mol). Conversions and selectivities were determined by gas chromatography using an internal standard technique and were based on hydrogen peroxide.













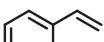
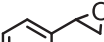
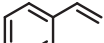
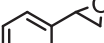

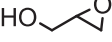

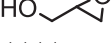














showed no catalytic activity (entry 16). The use of the homogeneous catalyst, $[\text{n-Bu}_4\text{N}]_7[\text{PW}_{11}\text{O}_{39}]$, (entry 15) under our reaction conditions also led to very high yield for epoxide.

In order to confirm BTE- $\text{PW}_{11}\text{O}_{39}$ was a heterogeneous catalyst, the solubility of the material was tested. BTE- $\text{PW}_{11}\text{O}_{39}$ was added into different solvents and heated at 60 °C for 1.5 h. Then the mixture was separated by filtration. The filtrates were tested by TLC and no fluorescence was observed. And then, to test leaching of the active POM composition in the solvents, cyclohexene and hydrogen peroxide were added into the filtrate, which were heated at 60 °C

for 1.5 h and showed no catalytic activity. The elemental analysis data of the reaction solution showed the concentration of P and W in reaction solvent was <1 µg/mL (1 ppm) and 25 µg/mL (25 ppm), respectively, indicating that leaching of the catalyst was quite minor. The material was insoluble in a wide array of solvents: DMF, DMSO, THF, acetonitrile, acetone, chlorinated hydrocarbons, hydrocarbons, alcohols and water.

The stability of the catalyst under catalytic conditions was tested by catalyst recycle-recovery experiments using cyclohexene as a model substrate (Fig. 2). The catalyst showed nearly quantitative conversion

Table 2
Epoxidation of various olefins catalyzed by BTE- $\text{PW}_{11}\text{O}_{39}$ with hydrogen peroxide.

Entry	Substrate	Product	Reaction time (h)	Selectivity (mol%)	Conversion (mol%)	TON
1			1.5	>99	93	129
2 ^a			4	>99	80	111
3			1.5	>99	96	133
4 ^a			2.5	>99	88	122
5			1.5	>99	99	137
6 ^a			7	95	96	126
7			5	54 ^b	93	70
8 ^a			8	74 ^b	49	50
9			6	>99	89	123
10 ^a			11	>99	83	115
11			19	>99	56	77
12 ^a			48	>99	19	26
13 ^c			12	>99	73	5400
14 ^c			10	>99	99	7300
15 ^d			1.5	>99	99	137
16 ^e			1.5	–	0	0
17 ^f			1.5	–	0	0

Reaction conditions: 2.5 mmol alkene; 0.5 mmol hydrogen peroxide; 3.6 µmol BTE- $\text{PW}_{11}\text{O}_{39}$; 0.75 mL acetonitrile; reaction temperature: 60 °C, conversion (%) = epoxide (mol)/hydrogen peroxide (mol). Selectivity (%) = epoxide (mol)/all products (mol). Conversions and selectivities were determined by gas chromatography using an internal standard technique and were based on hydrogen peroxide.

^a Reaction temperature: 30 °C.

^b Benzaldehyde was a co-product.

^c 25 mmol alkene; 5 mmol hydrogen peroxide; 0.67 µmol BTE- $\text{PW}_{11}\text{O}_{39}$; 7.5 mL acetonitrile; reaction temperature: 60 °C.

^d 4.6 µmol $[\text{n-Bu}_4\text{N}]_7[\text{PW}_{11}\text{O}_{39}]$.

^e 4.6 µmol BTE.

^f No catalyst was used.

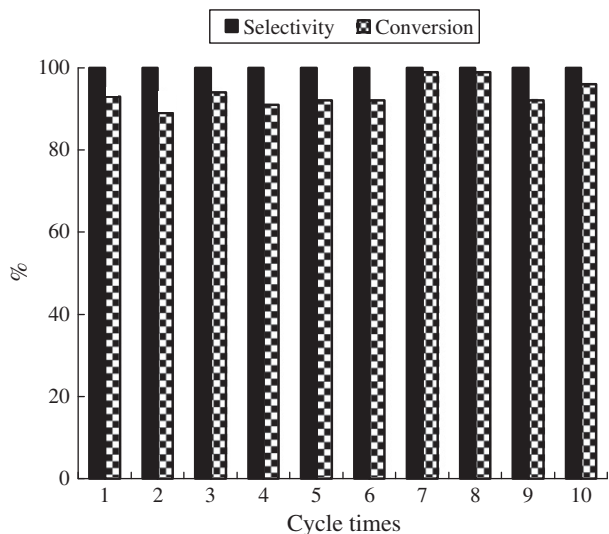


Fig. 2. Epoxidation of cyclohexene by BTE-PW₁₁O₃₉ for different cycles (a) conversion (b) selectivity. Reaction conditions: 2.5 mmol cyclohexene; 0.5 mmol hydrogen peroxide; 3.6 μmol BTE-PW₁₁O₃₉; 0.75 mL acetonitrile; reaction temperature: 60 °C, conversion (%) = epoxide (mol)/ hydrogen peroxide (mol). Selectivity (%) = epoxide (mol)/all products (mol). Conversions and selectivities were determined by gas chromatography using an internal standard technique and were based on hydrogen peroxide.

and selectivity to cyclohexene oxide over ten reaction cycles. The catalyst was recovered after each cycle by centrifugation. After the tenth catalytic cycle, no significant changes were observed in IR spectra (Fig. 1 (c), (d), (e)). However, the ³¹P MAS NMR spectra (Fig. 3) reveal that there are some structural changes for the catalyst after reaction. The peaks at −15.04 and −12.35 ppm could be attributed to BTE-PW₁₂O₄₀ and BTE-PW₁₁O₃₉. The peak at 1.21 ppm could be attributed to BTE-[(PO₄){WO(O₂)₂]₂{WO(O₂)₂(H₂O)}] [13]. And the peak at 6.84 ppm could be attributed to species with low W/P ratio [13].

A proposed reaction mechanism was given in Scheme 1. To begin with, BTE-PW₁₁O₃₉ reacted with hydrogen peroxide to produce peroxy species (A) [31] including [(PO₃(OH){WO(O₂)₂}]²⁻, [(PO₄){WO(O₂)₂]₂{WO(O₂)₂(H₂O)}]³⁻ and [(PO₄){WO(O₂)₂}]³⁻ [32]. The

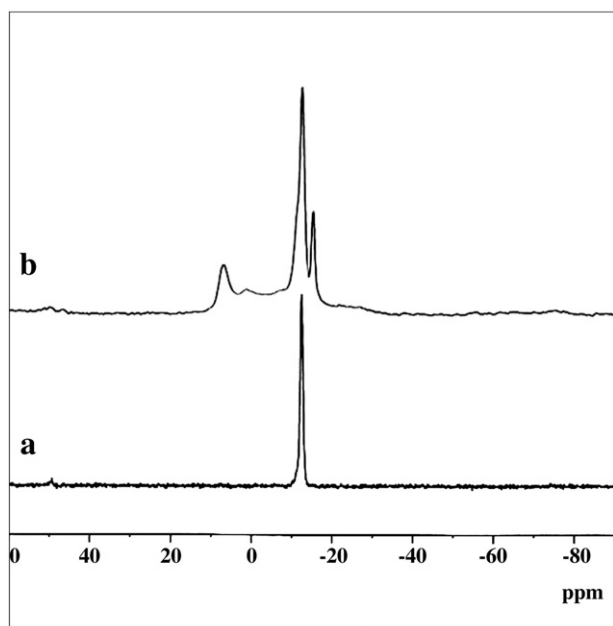


Fig. 3. ³¹P MAS NMR spectra of (a) the fresh catalyst of BTE-PW₁₁O₃₉; (b) the used BTE-PW₁₁O₃₉.

peroxy species reacted with the substrate and transferred active oxygen to the double bond of the alkenes. Since ³¹P MAS NMR of the used catalyst showed some structural changes, only a part of BTE-PW₁₁O₃₉ was recovered from the peroxy species again after finishing the reaction and other peroxy species produce BTE-PW₁₂O₄₀, BTE-[(PO₄){WO(O₂)₂]₂{WO(O₂)₂(H₂O)}] and species with low W/P ratio. We believed that BTE-PW₁₁O₃₉ did not like some homogeneous or phase-transferred controlled POMs catalysts which were dissolved in hydrogen peroxide under the reaction condition. When BTE-PW₁₁O₃₉ reacted with hydrogen peroxide, it just formed a peroxy species (A) which was insoluble in reaction solution. In order to prove this hypothesis, BTE-PW₁₁O₃₉ was treated with hydrogen peroxide simply without substrate in acetonitrile at 60 °C for 1.5 h. FT-IR of the material (Fig. 1 (c), (f)) which was treated with hydrogen peroxide showed the structure of the catalyst changed after reacted with hydrogen peroxide, which indicated that the activated complex (A) existed.

4. Conclusion

In summary, a heterogeneous catalytic material has been synthesized by preparing insoluble inorganic–organic hybrid compound based on a tripodal organic triammonium cation, BTE, and a catalytically active POM species, [PW₁₁O₃₉]⁷⁻. The catalytic system consisting of BTE-PW₁₁O₃₉/hydrogen peroxide/acetonitrile/olefin can efficiently catalyze many kinds of alkenes epoxidation in normal to good yields both at 60 °C and 30 °C. This active catalyst can be easily recovered and reused without loss of activity. So BTE-PW₁₁O₃₉ is a heterogeneous and reusable catalyst for the epoxidation of olefins.

Acknowledgements

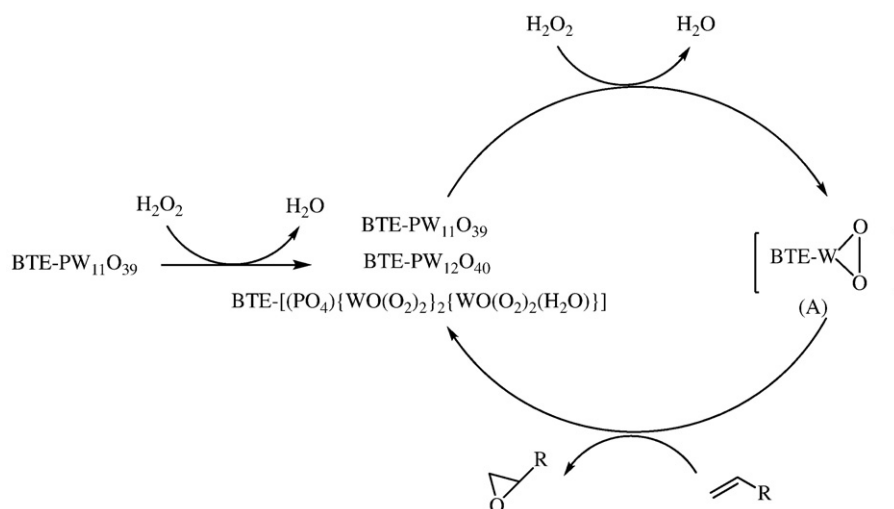
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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2010.09.026.

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Scheme 1. Proposed catalytic cycle for the epoxidation of olefin by $\text{BTE-PW}_{11}\text{O}_{39}$ with hydrogen peroxide as oxygen source.

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