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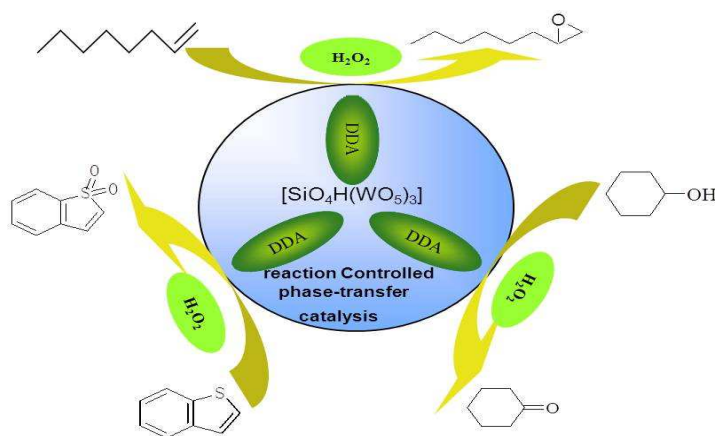
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## Graphic abstract

**A new halide-free efficient reaction-controlled phase-transfer catalyst based on silicotungstate of  $[(C_{18}H_{37})_2(CH_3)_2N]_3[SiO_4H(WO_5)_3]$  for olefin epoxidation, oxidation of sulfides and alcohols with hydrogen peroxide**

Baochun Ma<sup>a\*</sup>, Wei Zhao<sup>b</sup>, Fuming Zhang<sup>a</sup>, Yingshuai Zhang<sup>a</sup>, Songyun Wu<sup>a</sup>, Yong Ding<sup>a</sup>



A new environmentally benign and highly efficient reaction-controlled phase-transfer catalyst for olefin epoxidation, sulfides and alcohols oxidation was developed.

# A new halide-free efficient reaction-controlled phase-transfer catalyst based on silicotungstate of $[(C_{18}H_{37})_2(CH_3)_2N]_3[SiO_4H(WO_5)_3]$ for olefin epoxidation, oxidation of sulfides and alcohols with hydrogen peroxide

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

First published on the web Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

A new reaction-controlled phase-transfer catalyst based on silicotungstate of  $[(C_{18}H_{37})_2(CH_3)_2N]_3[SiO_4H(WO_5)_3]$  for oxidation of hydrocarbons is developed. The catalyst is a new heteropoly compound with silicon as heteroatom, which is different to the previously reported reaction-controlled phase transfer catalysts that were composed of quaternary ammonium heteropolyoxotungstates of  $[\pi-C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{16}]$  and  $[\pi-C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{32}]$  with phosphorus as heteroatom. The oxidation of various alkenes (such as linear terminal olefins, internal olefins, cyclic olefins and unactivated alkenes) to epoxides, sulfides to sulfoxides and sulfones, alcohols to the carbonyl compounds, are successfully catalyzed by this recyclable and environmentally benign catalyst using  $H_2O_2$  as oxidant and ethyl acetate as solvent. This catalyst is not only capable of catalyzing homogeneous oxidation of organic substrates with unique reaction-controlled phase-transfer character, but also avoids the using of toxic solvents. The catalyst could be easily recovered and reused after reaction, and the epoxidation of cyclohexene was recycled twenty times without obvious loss in activity. The fresh catalyst and the used one were characterized by ICP, IR, UV-vis,  $^{29}Si$  MAS NMR and  $^{183}W$  NMR in details.

## Introduction

Epoxides are highly useful intermediates for the manufacture of a range of important commercial products, and epoxidation of alkenes is among the most important reactions in organic synthesis<sup>1-4</sup>. A catalytic epoxidation system that uses hydrogen peroxide as a oxidant is very attractive from the viewpoint of industrial production and synthetic organic chemistry since aqueous hydrogen peroxide is cheap, environmentally clean and easy to handle<sup>5-8</sup>. The chemistry of polyoxometalates (POMs) has drawn wide attention in the last two decades as effective catalysts for epoxidation of alkenes<sup>8-27</sup>. The groups of Venturello<sup>15, 16</sup> and Ishii<sup>17, 27</sup> independently developed highly effective tungstophosphate-based catalyst systems for alkene epoxidation with hydrogen peroxide. However, toxic and carcinogenic chlorocarbons (chloroform and 1, 2-dichloroethane) were used as solvents in their systems. Later, Mizuno<sup>18-21</sup> developed a series of silicotungstate polyoxometalates as efficient catalysts for alkene epoxidation, such as  $(Bu_4N)_4[\gamma-SiW_{10}O_{34}(H_2O)_2]$  and  $(Bu_4N)_4[\gamma-1,2-H_2SiV_2W_{10}O_{40}]$ . Both the activities and selectivities of these homogeneous catalytic epoxidation of olefins with  $H_2O_2$  were excellent. However, there was a common problem for the difficulty in separation and reuse of catalysts in these homogeneous catalytic systems.

The searching for more efficient catalytic systems that combine the advantages of both homogeneous and heterogeneous catalysis is one of the most exciting challenges of modern chemistry. 2001, Xi<sup>22-24</sup> reported a reaction-controlled phase-transfer catalyst  $[\pi-C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{16}]$  based on quaternary ammonium

heteropolyoxotungstates, which exhibited high conversion and selectivity for catalytic epoxidation of olefins. After reaction, the catalyst can be recovered and reused just like a heterogeneous catalyst by filtration. 2008, our group<sup>8, 26</sup> reported another efficient reaction-controlled phase-transfer catalytic system based on quaternary ammonium heteropolyoxotungstate of  $[\pi-C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{32}]$ . The above reaction-controlled phase-transfer catalysts were both based on polyoxometalate of which the heteroatom was phosphorus. Does tungsten-based polyoxometalate catalyst with silicon as the heteroatom has the reaction-controlled phase-transfer catalytic character?

In an attempt to interpret and address this question, we investigated the epoxidation of 1-octene with  $H_2O_2$  catalyzed by a series of silicotungstates in ethyl acetate at 333 K as model tests. After screening many different silicotungstates, we found that a dioctadecyl dimethyl ammonium (DDA) salt of silicotungstate,  $[(C_{18}H_{37})_2(CH_3)_2N]_3[SiO_4H(WO_5)_3]$  (I) showed good catalytic activity over the epoxidation of various alkenes with the reaction-controlled phase-transfer feature that could be recovered and reused just like a heterogeneous catalyst after reaction. The epoxidation was conducted in ethyl acetate, and many kinds of alkenes could be converted to the corresponding epoxides in high yields. In an aqueous  $H_2O_2$ /ethyl acetate biphasic system, catalyst I itself was not soluble in the ethyl acetate phase, but it dissolved slowly with the increasing of reaction temperature and with the addition of hydrogen peroxide, which subsequently led to homogeneous catalytic system for epoxidation of olefins. When the reaction finished with the decrease of temperature, catalyst I precipitated as a white solid from the solvent

gradually. This phenomenon manifested a solid-liquid-solid phase transfer of catalyst I controlled by the reaction conditions in ethyl acetate. Various sulfides and alcohols were also transformed into their corresponding oxidative forms over this reaction-controlled phase-transfer catalyst.

## Experimental

### Reagents

All chemicals were analytical grade, commercially available and used without further purification unless otherwise stated.

### 10 Characterization techniques

Infrared spectra of heteropolyoxotungstates were recorded on a Nicolet NEXUS 670 FT-IR spectrometer. The  $^{183}\text{W}$  NMR spectra were recorded in 5 mm o.d. tubes enclosed a capillary filled with  $\text{C}_6\text{D}_6$ . The  $^{183}\text{W}$  chemical shifts were measured with respect to an external 2 M  $\text{Na}_2\text{WO}_4$  solution in alkaline  $\text{D}_2\text{O}$  by using dodecaphosphotungstic salt of  $[\pi\text{-C}_3\text{H}_5\text{N}(\text{CH}_2)_{11}\text{CH}_3]_3[\text{PW}_{12}\text{O}_{40}]$  in dichloromethane solution as a secondary standard ( $\delta$  -85.0 ppm).  $^{29}\text{Si}$  MAS NMR spectra were recorded at 9.4 T on a Bruker Avance-400 wide bore spectrometer. The  $^{29}\text{Si}$  MAS NMR spectra of solid catalyst with cross-polarization were performed at 79.5 MHz with BB (broad band) MAS probe head using 4 mm  $\text{ZrO}_2$  rotors and 2 ms constant time and 3 s repetition time and 11600 scans, with samples spun at 10 kHz and referenced to  $\text{SiMe}_4$ . Chemical elemental analysis of the catalysts was done as follows: Si, W content was analyzed by PE 4300 DV ICP-AES spectrometer. C, H, and N contents were measured on a German Elementar Vario EL spectrometer. GC analysis was performed on Shimadzu GC-9AM with a flame ionization detector equipped with SE-54 capillary (internal diameter = 0.25 mm, length = 30 m). GC-MS were recorded on Finnigan Trace DSQ (Thermo Electron Corporation) at an ionization voltage of 70 eV equipped with a DB-5 capillary column (internal diameter = 0.25 mm, film thickness = 0.25  $\mu\text{m}$ , length = 30 m).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-400 and Varian mercury 300 MHz spectrometer with TMS as an internal standard and  $\text{CDCl}_3$  as solvent unless otherwise noted.

### Preparation of the catalyst

$\text{K}_8$   $[[\beta_2\text{-SiW}_{11}\text{O}_{39}]\cdot 14\text{H}_2\text{O}]$  and  $\text{K}_8$   $[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O}$  were synthesized according to ref<sup>28</sup>.

$[(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}]_3[\text{SiO}_4\text{H}(\text{WO}_5)_3]$ :

$\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O}$  (2.5 g, 0.85 mmol) was dissolved in 40 ml 30%  $\text{H}_2\text{O}_2$  ( $\text{H}_2\text{O}_2 / \text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O} = 450 \text{ mol} / 1 \text{ mol}$ ) and the solution was stirred for 4 h at room temperature. Then 48 ml 30%  $\text{H}_2\text{O}_2$  ( $\text{H}_2\text{O}_2 / \text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O} = 550 \text{ mol} / 1 \text{ mol}$ ) was added to the above solution. Subsequently, to this solution, 1 g (1.7 mmol) of dioctadecyl dimethyl ammonium chloride (DDAC) dissolved in 25 ml of tert-butanol was added. The mixture was stirred vigorously for 4 h at 318 K. A white floccule was filtered off and then washed with an excess amount of warm water ( $\sim 318 \text{ K}$ , about 100 ml) and dried in vacuum.  $[(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}]_3[\text{SiO}_4\text{H}(\text{WO}_5)_3]$  was obtained as a white powder. Yield: 1.1 g (75%, based on

the quaternary ammonium salt charged). Anal. calcd for  $[(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}]_3[\text{SiO}_4\text{H}(\text{WO}_5)_3]$ : C, 53.98; H, 9.51; N, 1.66; Si, 1.10; W, 21.76; Found: C, 52.42; H, 9.51; N, 1.75; Si, 1.09; W, 21.23. IR spectrum (KBr,  $\text{cm}^{-1}$ ): 2921, 1717, 1467, 1088, 1055, 1000, 967, 942, 846, 722, 634, 574, 511, 473, 448. UV-vis spectrum (in  $\text{CDCl}_3$ ) showed shoulder bands at 243 nm.  $^{29}\text{Si}$  MAS NMR (79.5 MHz): -79.2 ppm.  $^{183}\text{W}$  NMR (16.6 MHz,  $\text{CDCl}_3$ , 300K): -316 ppm.

Active oxygen was 1.7% in our catalyst  $[(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}]_3[\text{SiO}_4\text{H}(\text{WO}_5)_3]$ . Active oxygen was analyzed by the improved iodometric method proposed by Venturello<sup>16</sup>.

Other polyoxometalates preparation methods see the supporting information.

### Catalytic reaction

The catalytic reactions were performed in a 10 ml round-bottomed flask, a magnetic stirring bar, and a reflux condenser. The epoxidation was carried out as follows: catalyst (10  $\mu\text{mol}$ ), solvent (2 ml), substrate (2.5 mmol), and  $\text{H}_2\text{O}_2$  (30% aq., 0.5 mmol) were charged in the reaction flask. The reaction was carried out at 333 K and detected by TLC accompanied with GC. The yields of products were calculated from the peak areas using an internal standard method by GC. The products were identified by GC/MS (Finnigan Trace DSQ). After reaction (reaction temperature decreased to room temperature), the solid catalyst precipitated from the solvent and was separated by centrifugation. The recovered catalyst can be used for the next epoxidation after the treat with wash and dry.

The reactor for epoxidation of propylene was a 250ml Teflon coated steel autoclave and the reaction was carried out as follows: catalyst (0.185mmol), ethyl acetate (100ml),  $\text{H}_2\text{O}_2$  (30% aq., 20 mmol) and propylene (4 atm) were charged in the autoclave. The reaction was maintained at 333K for 2 hours. Resulting products were applied to GC analysis.

For the characterization and purity epoxidation products of dienes as follows:

The precipitate was removed by centrifugation and filtration, and the filtrate extracted with  $\text{EtOAc}$  (30ml x 3), the organic layer was collected and washed with water and brine, then dried with anhydrous  $\text{Na}_2\text{SO}_4$ . After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography with eluent (petroleum ether/ethyl acetate 10/1) to give epoxides as colorless liquid. The structures of the epoxides were determined by MS (EI),  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR.

## Results and discussion

### Epoxidation of various olefins

Epoxidation of 1-octene was carried out with various polyoxometalates including saturated and lacunary polyoxometalates in ethyl acetate at 333 K (Table 1). Compound I exhibited the highest activity among all the catalysts (entry 1) and showed a 97% yield of 1, 2-epoxyoctane. Saturated silicotungstate of  $[(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}]_4[\text{SiW}_{12}\text{O}_{40}]$  and saturated

tungstophosphate of  $[(C_{18}H_{37})_2(CH_3)_2N]_3[PW_{12}O_{40}]$  showed no activity (entry 2-3). Dioctadecyl dimethyl ammonium salt of the other lacunary silicotungstates and peroxotungstate showed poor activity (entry 4-6), and these catalysts were not soluble in ethyl acetate even at 333 K. As shown in Table 1, no epoxide was detected for the simple mixture of dioctadecyl dimethyl ammonium chloride (DDAC),  $Na_2WO_4 \cdot 2H_2O$  and  $Na_2SiO_3 \cdot 9H_2O$ , or the mixture of two of them (entry 8-11). The epoxidation can not proceed without catalyst (entry 12). When only catalyst I was added without  $H_2O_2$ , the yield of 1, 2-epoxyoctane was 2% (entry 13). The producing of 1-octene oxide should be ascribed to the peroxo species in the catalyst and further confirmed the existence of peroxo v(O-O) band in compound I.

Table 1. Epoxidation of 1-octene with  $H_2O_2$  catalyzed by various catalysts<sup>a</sup>

| Entry           | Catalyst   | Selectivity (mol%). | Yield (mol%) |
|-----------------|--|---------------------|--------------|
| 1               | I  | 99                  | 97           |
| 2               | [DDA] <sub>4</sub> [SiW <sub>12</sub> O <sub>40</sub> ]  | 0                   | 0            |
| 3               | [DDA] <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ]   | 0                   | 0            |
| 4               | [DDA] <sub>8</sub> [β <sub>2</sub> -SiW <sub>11</sub> O <sub>39</sub> ]                                      | 99                  | 8            |
| 5               | [DDA] <sub>8</sub> [γ-SiW <sub>10</sub> O <sub>36</sub> ]  | 99                  | 8            |
| 6               | [DDA] <sub>2</sub> [W <sub>3</sub> O <sub>18</sub> ]   | 99                  | 17           |
| 7 <sup>b</sup>  | [(C <sub>18</sub> H <sub>37</sub> ) <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> N]Cl                        | 0                   | 0            |
| 8 <sup>c</sup>  | Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O+Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O+ DDAC | 0                   | 0            |
| 9 <sup>d</sup>  | Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O+ Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O      | 0                   | 0            |
| 10 <sup>e</sup> | Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O+ DDAC  | 0                   | 0            |
| 11 <sup>f</sup> | Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O+ DDAC   | 0                   | 0            |
| 12              | No Catalyst  | 0                   | 0            |
| 13 <sup>g</sup> | No H <sub>2</sub> O <sub>2</sub>   | 99                  | 2            |

<sup>a</sup> Reaction conditions: 2.5 mmol 1-octene; 0.5 mmol  $H_2O_2$ ; 10 μmol catalyst; 2 ml ethyl acetate; reaction temperature: 333 K, reaction time: 3 h. Selectivity (%) = epoxide (mol)/all products (mol) × 100. Yield (%) = epoxide (mol)/ $H_2O_2$  used (mol) × 100. Conversions and selectivities were determined by gas chromatography using an internal standard technique and were based on  $H_2O_2$ . <sup>b</sup> [(C<sub>18</sub>H<sub>37</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>N]Cl = Dioctadecyl dimethyl ammonium chloride (DDAC), 30 μmol. <sup>c</sup> 10 μmol Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O, 30 μmol Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, 30 μmol DDAC. <sup>d</sup> 10 μmol Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O, 30 μmol Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O. <sup>e</sup> 10 μmol Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O, 30 μmol DDAC. <sup>f</sup> 20 μmol Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, 60 μmol DDAC. <sup>g</sup> Yield (%) = alkenes' conversion × epoxide selectivity.

To study the solvent effect of the reaction-controlled phase-transfer catalytic system, the epoxidation of 1-octene with  $H_2O_2$  using catalyst I was carried out at the same temperature (333K) with different solvents (Table 2). Epoxidation of cyclohexene catalyzed by I with  $H_2O_2$  in ethyl acetate at 333 K resulted in 99% selectivity and 96% yield. Those solvents of tert-butanol, acetonitrile, dioxane, toluene, 1,2-dichlorethane and cyclohexane gave lower yields for the epoxidation of cyclohexene. Although catalyst I was soluble in toluene, 1,2-dichlorethane and cyclohexane during reaction, the catalyst could not be precipitated out from those solvents when temperature dropped from 333 K to 298 K. In tert-butanol and dioxane, the phenomena of solid-liquid-solid phase transfer of catalyst I existed, but the amount of the

catalyst precipitate was very little, indicating the two solvents were not suitable for recovering catalyst. Based on the above results, ethyl acetate is the best candidate solvent. Solvents have effect on forming an efficient reaction-controlled phase-transfer catalytic system.

Table 2. Epoxidation of cyclohexene catalyzed by I under different solvents<sup>a</sup>

| Entry | Solvent            | Selectivity (mol%) | Yield (mol%) |
|-------|--------------------|--------------------|--------------|
| 1     | Ethyl acetate      | 99                 | 96           |
| 2     | tert-Butanol       | 99                 | 84           |
| 3     | Acetonitrile       | 99                 | 82           |
| 4     | Dioxane            | 99                 | 81           |
| 5     | Toluene            | 99                 | 78           |
| 6     | 1,2-dichloroethane | 99                 | 79           |
| 7     | Cyclohexane        | 99                 | 70           |
| 8     | Ethanol            | 99                 | 45           |

<sup>a</sup> Reaction conditions: 2.5 mmol cyclohexene; 0.5 mmol  $H_2O_2$ ; 10 μmol catalyst of I; 2 ml solvent; reaction temperature: 333 K, reaction time: 2 h. Selectivity (%) = cyclohexene epoxide (mol)/all products (mol) × 100. Yield (%) = cyclohexene epoxide (mol)/ $H_2O_2$  used (mol) × 100. Conversions and selectivities were determined by gas chromatography.

The silicotungstate catalyst I is applicable to the epoxidation of various olefins (such as linear terminal olefins, internal olefins, cyclic olefins and unactivated alkenes) with 30%  $H_2O_2$ , and high yields and selectivities are achieved (Table 3). The same phenomena of reaction-controlled phase-transfer catalysis were observed all in these epoxidations, and excellent catalytic activities were presented. Bulky cyclic olefins such as cyclohexene, 1-methyl-cyclohexene, cyclooctene and norbornene were epoxidized with 99% selectivity and ~90% yield of epoxides (entry 1-5).

Nonactivated terminal C<sub>7</sub>-C<sub>16</sub> olefins, such as 1-heptene, 1-octene, 1-undecene, 1-dodecene and 1-hexadecylene, could be transformed to the corresponding epoxides specifically with 99% selectivity and ~90% yield of epoxides (entry 12-17). For epoxidation the gas of propylene, a 94% selectivity and 90% yield of epoxide (entry 18) were obtained in 2 hours at 333 K, in which the reaction time is far shorter than that of Xi's reaction-controlled phase-transfer catalyst (5 hours at 338K)<sup>22</sup>. Therefore, the catalytic performance of this reaction-controlled phase-transfer catalyst inspires the prospect of using this type of catalyst for the industrial epoxidation of propylene instead of the classical chlorohydrin process. In the latter status, epoxides are usually consecutively hydrated and the oxirane ring is cleaved, resulting in a decrease in selectivity. Furthermore, large amounts of Cl<sub>2</sub> are consumed for the classical chlorohydrin process, which gives rise to serious problems of equipment corrosion and environmental pollution.

Those olefins containing aromatic group, such as styrene, α-methylstyrene and indene, were also converted to corresponding epoxides selectively, while a small amount of benzaldehyde or corresponding aromatic aldehyde was formed (entry 6-8). Epoxidation rate of 2-heptene was faster than that of 1-heptene, and the configuration of the C=C bond was

**Table 3** Epoxidation of various olefins with H<sub>2</sub>O<sub>2</sub> catalyzed by I<sup>a</sup>

| Entry           | Substrate | Product | Reaction time (h) | Selectivity (mol%) | Yield (mol%) |
|-----------------|-----------|---------|-------------------|--------------------|--------------|
| 1 <sup>b</sup>  |           |         | 2                 | 99                 | 88           |
| 2               |           |         | 2                 | 99                 | 96           |
| 3               |           |         | 2                 | 99                 | 99           |
| 4               |           |         | 2                 | 99                 | 97           |
| 5               |           |         | 1                 | 99                 | 99           |
| 6               |           |         | 3                 | 92                 | 92           |
| 7               |           |         | 2                 | 94                 | 94           |
| 8               |           |         | 3                 | 94                 | 94           |
| 9               |           |         | 2                 | 99                 | 84           |
| 10              |           |         | 7                 | 99                 | 65           |
| 11              |           |         | 7                 | 99                 | 62           |
| 12              |           |         | 2                 | 99                 | 99           |
| 13              |           |         | 3                 | 99                 | 98           |
| 14              |           |         | 3                 | 99                 | 97           |
| 15              |           |         | 3                 | 99                 | 93           |
| 16              |           |         | 2                 | 99                 | 92           |
| 17              |           |         | 3                 | 99                 | 99           |
| 18 <sup>c</sup> |           |         | 2                 | 94                 | 90           |

<sup>a</sup> Reaction conditions: 2.5 mmol alkene; 0.5 mmol H<sub>2</sub>O<sub>2</sub>; 10 μmol catalyst of I; 2 ml ethyl acetate; reaction temperature: 333 K, Selectivity (%) = epoxide (mol)/all products (mol) × 100. Yield (%) = epoxide (mol)/H<sub>2</sub>O<sub>2</sub> used (mol) × 100. Conversions and selectivities were determined by gas chromatography using an internal standard technique and were based on H<sub>2</sub>O<sub>2</sub>. <sup>b</sup> Reaction temperature: 318 K. <sup>c</sup> Propylene 4 atm, 2 ml 30% H<sub>2</sub>O<sub>2</sub>

retained in the corresponding epoxide (cis-2, 3-epoxyheptane was obtained with a 99% yield). In general, the epoxidation of allylic alcohol and allylic chloride are carried out difficultly compared with those of cyclic olefin, since the C=C double bond in allyl moieties is relatively electron deficient by the electron-withdrawing group of hydroxyl (-OH) and -Cl. In our catalytic system, a 84% yield of 2,3-epoxy-1-propanol and 65% yield of epichlorohydrin were obtained over catalyst I (entry 9-10) at 333 K, respectively, revealing this epoxidation system was effective and fairly universal to all kinds of alkenes.

This new green process of epoxidation is also effective for the epoxidation of dienes (Table 4). After two hours reaction, 90 % conversion for all substrates was obtained, but the selectivity for monoepoxide was moderate. Limonene and 4-vinyl-1-cyclohexene, a C=C moiety with higher electron density was epoxidized regioselectively to give the corresponding monoepoxide without the successive epoxidation of the other C=C fragment (entry 1-2) (similar to these catalysts of [TBA]<sub>4</sub>[γ-SiW<sub>10</sub>O<sub>34</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>21</sup> and [π-C<sub>5</sub>H<sub>5</sub>N(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>]<sub>3</sub>[PW<sub>4</sub>O<sub>32</sub>]<sup>8</sup>). Dicyclopentadiene and

geraniol were displayed moderate selectivity for monoepoxide (selectivity to monoepoxide was ~ 70%, entry 3-4). When 1-methyl-1,4-cyclohexadiene were epoxidized (entry 5), it gave an equal products distribution for the monoepoxide of 3-methyl-7-oxa-bicyclo[4.1.0]hept-3-ene (49% yield) and 1-methyl-7-oxa-bicyclo[4.1.0]hept-3-ene (46% yield).

**Table 4** Epoxidation of dienes with H<sub>2</sub>O<sub>2</sub> catalyzed by I<sup>a</sup>

| Entry | dienes | product | Selectivity (mol%) | Yield (mol%) |
|-------|--------|---------|--------------------|--------------|
| 1     |        |         | 99                 | 99           |
| 2     |        |         | 95                 | 84           |
| 3     |        |         | 30                 | 30           |
| 4     |        |         | 69                 | 69           |
| 5     |        |         | 28                 | 28           |
|       |        |         | 72                 | 71           |
|       |        |         | 49                 | 49           |
|       |        |         | 46                 | 46           |

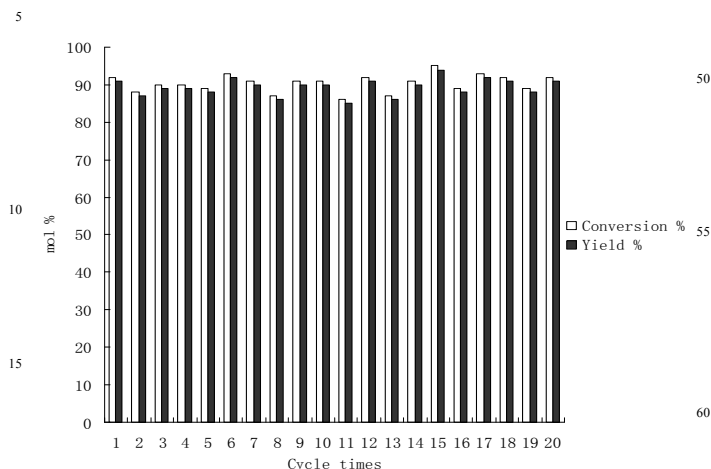
<sup>a</sup> Reaction conditions: 2.5 mmol alkene; 0.5 mmol H<sub>2</sub>O<sub>2</sub>; 10 μmol catalyst of I; 2 ml ethyl acetate; reaction temperature: 333 K, reaction time: 2 h. Selectivity (%) = monoepoxide (mol)/all products (mol) × 100. Yield (%) = epoxide (mol)/H<sub>2</sub>O<sub>2</sub> used (mol) × 100. Conversions and selectivities were determined by gas chromatography using an internal standard technique and were based on H<sub>2</sub>O<sub>2</sub>. The products were identified by GC/MS and <sup>1</sup>H NMR.

### Reuse of catalyst

Another notable feature of this reaction-controlled phase-transfer catalytic system is that the recovery and reuse of the catalyst I was very efficient, easy and convenient. Since the epoxidation was carried out in solid-liquid-solid phase transfer mode, the solid catalyst could be easily recovered by filtration or centrifugation and reused after reaction. The recycling experiments over epoxidation of cyclohexene were shown on Figure 1. The yield of cyclohexene epoxide did not drop even after twenty consecutive cycles, a 90% yield of the epoxide with 99% selectivity was still kept for the epoxidation of cyclohexene. No fresh catalyst I was added and no reaction time was prolonged.

To evaluate the recycling capability of this reaction-controlled phase-transfer catalytic system, another substrate of 1-octene that typically inert substrate to be epoxidized was investigated for epoxidation research (Table S1). We found the solubility of silicotungstate catalyst I in 1-octene/ethyl acetate was better than that in cyclohexene/ethyl acetate, so the loss of catalyst for the former was more severely than that for the later. The recovery of catalyst in 1-octene/ethyl acetate

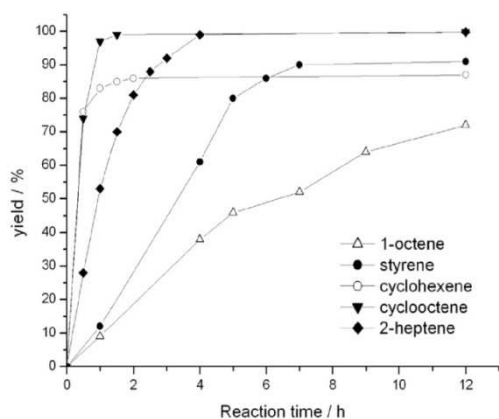
was not as good as that in cyclohexene/ethyl acetate. However, it was exciting that the yield of epoxide still kept more than 80% even after twenty consecutive cycles. No fresh catalyst I was added and only reaction time was prolonged.



**Fig.1** epoxidation of cyclohexene on catalyst I. Reaction conditions: 5 mmol alkene; 1 mmol  $\text{H}_2\text{O}_2$ ; 20  $\mu\text{mol}$  catalyst of I; 4 ml ethyl acetate; reaction temperature: 60  $^\circ\text{C}$ , reaction time: 2 h. Conversion (%) = products (mol)/ $\text{H}_2\text{O}_2$  used (mol)  $\times 100$ . Yield (%) = epoxide (mol)/ $\text{H}_2\text{O}_2$  used (mol)  $\times 100$ . Selectivity of cyclohexene epoxide was more than 99% for all cycles.

### Kinetics of the epoxidation

The kinetics of epoxidation of some typical alkenes with 30% hydrogen peroxide catalyzed by I were investigated in the stoichiometric condition between the oxidant and the substrates (Fig. 2). The catalyst I shows best activity for epoxidation of cyclooctene, a 99% yield of epoxide was obtained in 1 hour. For 2-heptene, it took 4 hours to get the same yield (99%) of 2-heptene oxide. The initial reaction rate of cyclohexene catalyzed by I was nearly the same as that of cyclooctene, but the yield of cyclohexene oxide was 85% in

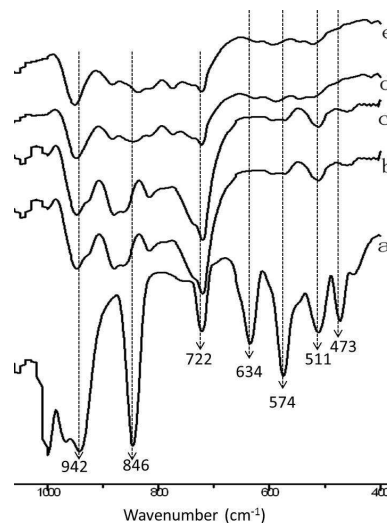


**Fig.2** Reaction profiles for the epoxidation of different olefins with one equivalent of 30% hydrogen peroxide catalyzed by I. Reaction conditions: 0.5 mmol alkene; 0.5 mmol  $\text{H}_2\text{O}_2$ ; 20  $\mu\text{mol}$  catalyst of  $[(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}]_3[\text{SiO}_4\text{H}(\text{WO}_5)_3]$ ; 2 ml ethyl acetate; reaction temperature: 333K. Conversions and selectivity were determined by gas chromatography using an internal standard technique.

one hour. After that, it levelled off when the reaction time was prolonged. The initial reaction rate of styrene was far lower than that of cyclohexene, but after 7 hours reaction, the final styrene oxide yield (90%) was higher than that of cyclohexene oxide. The linear terminal olefin substrate of 1-octene was the most difficult to be epoxidized among them, even after 12 hours reaction, only 70% yield of epoxide was obtained. All the epoxidations catalyzed by I showed no induction period, which is different to the polyoxometalate of  $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]$  that showed an induction period of approximately 60 min during the epoxidation of cyclooctene<sup>21</sup>.

### Characterization analysis

The FT-IR spectrum of the fresh catalyst I (Fig. 3a) gave bands at 1000, 967, 942, 846, 722, 634, 574, 511, 473 and 448  $\text{cm}^{-1}$  in the fingerprint region. The IR of 574, 846, 942 and 967  $\text{cm}^{-1}$  can be assigned to  $\nu(\text{W}(\text{O}_2))$ ,  $\nu(\text{O}-\text{O})$ ,  $\nu(\text{Si}-\text{OH})$  and  $\nu(\text{W}=\text{O})$  [20, 26], respectively. The presence of 846  $\text{cm}^{-1}$

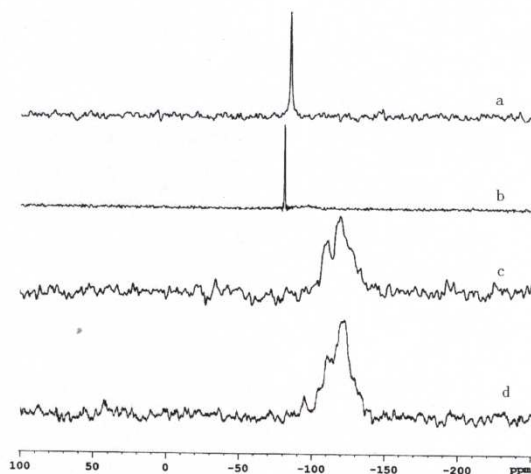


**Fig.3** FT-IR spectra of (a) the fresh catalyst of Catalyst I; (b) the used catalyst for cycle 1; (c) the used catalyst for cycle 2; (d) the used catalyst for cycle 3; (e) the used catalyst for cycle 5.

proves that there exists peroxy  $\nu(\text{O}-\text{O})$  band in the compound of silicotungstate I. Compared with the IR spectra of fresh catalyst and used one, the bands of them are different and the used catalyst has converted into another species (named as silicotungstate II). However, since the catalyst began to recycle, the IR spectra of the first, second, third and fifth recycled ones show nearly the same bands (Fig. 3 b, c, d and e). The similarity of IR spectra among the recycled catalysts indicates that the structure of dioctadecyl dimethyl ammonium salt of silicotungstate catalyst II has not changed and it was stable during the catalytic cycles from the second catalytic cycle. Furthermore, the  $^{29}\text{Si}$  MAS NMR spectra of fresh and used catalysts are nearly the same (Fig. 4c, d), indicating the catalyst keeps stable from second cycle. So, the silicotungstate I should be called pre-catalyst accurately. The used catalyst after first run is the true catalyst and is named as silicotungstate II. The high activity was maintained for many cycles should be attributed to the stable structure of the

recycled catalysts.

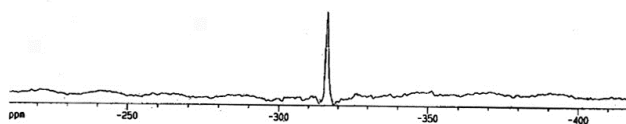
The  $^{29}\text{Si}$  MAS NMR spectrum of silicotungstate I showed one signal at -79.2 ppm (Fig. 4b), which is different to that of known silicotungstates, such as  $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$  (-85.0 ppm) (Fig. 4a) and  $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$  (-84.4 ppm)<sup>29</sup>, suggesting that I is a new pure silicotungstate compound.



**Fig. 4**  $^{29}\text{Si}$  MAS NMR spectra of catalysts: a)  $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O}$ ; b)  $[(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}]_3[\text{SiO}_4\text{H}(\text{WO}_5)_3]$ ; c) the catalyst of cycle 1; d) the catalyst of cycle 2.

The NMR signal of this silicotungstate complex moves toward downfield and is similar to the wellknown Venturolo peroxocomplex of  $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$  (or  $[\text{PW}_4\text{O}_{24}]^{3-}$ ), derived from the decomposition of  $\text{Q}_3[\text{PW}_{12}\text{O}_{40}]$ , which also shifts from upfield ( $\sim -14$ -15 ppm) to downfield ( $\sim -3$ -4 ppm)<sup>14</sup>.

While the  $^{29}\text{Si}$  MAS NMR spectrum of used catalyst (II) gives several broad peaks whose chemical shift moves toward upfield, ranging from -115 ppm to -130 ppm (Fig. 4c, d). The original single peak at -79.2 ppm for I has disappeared. The new broad peaks for the used catalyst II suggest that the catalyst is a mixture that contains several different silicotungstate species. It can be seen that the  $^{29}\text{Si}$  MAS NMR spectra of used catalyst for cycle 1 and cycle 2 are nearly same (Fig. 4c, d), revealing that the structure of these used catalysts are same and the catalyst keeps stable from the catalytic cycles.

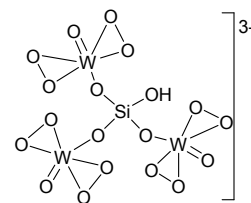


**Fig. 5**  $^{183}\text{W}$  NMR spectrum of catalyst I (16.6 MHz,  $\text{CDCl}_3$ , 300K).

The  $^{183}\text{W}$  NMR spectrum of I in  $\text{CDCl}_3$  shows one signal at -316 ppm (Fig. 5), which is different to that of other reported catalytically peroxotungstate<sup>30</sup>, such as  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\{\text{WO}(\text{O}_2)_2\}_2(\mu\text{-O})]$  (-587.5 ppm) and silicotungstate of  $(\text{Bu}_4\text{N})_4[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]$ <sup>21</sup> ( $^{183}\text{W}$  NMR showed five signals at  $\delta = -95.7, -98.9, -118.2, -119.6,$  and  $-195.7$  ppm). The single signal of  $^{183}\text{W}$  NMR of I indicates that

the chemical environment of the three tungsten atoms in compound I is identical.

The elemental analysis of I showed that the dioctadecyl dimethyl ammonium:Si:W mol ratio is 3:1:3. The UV-vis spectrum of I in  $\text{CHCl}_3$  shows an absorption band at 243 nm (Fig. S3), which is the characteristic band of the peroxotungstate<sup>31</sup>. The characteristic IR band of the  $\nu(\text{W-O}_b\text{-W})$  (corner-sharing) and  $\nu(\text{W-O}_c\text{-W})$  (edge-sharing) in polymerization of W species of Keggin polyoxometalate should be in the range of 870-880 and 780-790  $\text{cm}^{-1}$ <sup>32</sup>, respectively. However, those bands are not observed in the FT-IR spectrum of I, suggesting the absence of polymerization of W species in catalyst I. The characteristic band of  $\nu(\text{Si-OH})$ <sup>33</sup> at 942  $\text{cm}^{-1}$  is observed in the IR spectrum of I. Based these results, we proposed a structure of I may be  $[(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}]_3[(\text{OH})\text{SiO}_3\{\text{WO}(\text{O}_2)_2\}_3]$  (Scheme 1), which is similar to the well known Venturolo complex of  $[\{\text{W}(\text{=O})(\text{O}_2)_2\}_4(\mu\text{-PO}_4)]^{3-}$ . Unfortunately, even tried our best, we did not obtain crystallographic quality single crystals of catalyst I in various solvents with vapor diffusion of poor solvents (such as diethyl ether and methanol) so far. Therefore, the precise structural formula of I can not be given so far.



**Scheme 1** Proposed structure of the anion of I:  $[(\text{OH})\text{SiO}_3\{\text{WO}(\text{O}_2)_2\}_3]^{3-}$

### Mechanism of the epoxidation of olefin by I

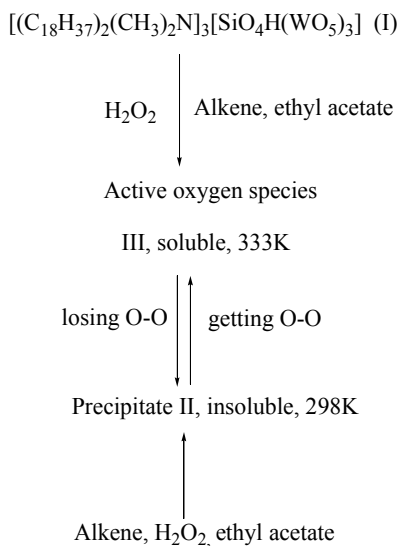
On the basis of all the results, we propose a reaction mechanism for the epoxidation of olefins with hydrogen peroxide catalyzed by I (Scheme 2). First, when pre-catalyst of  $[(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}]_3[\text{SiO}_4\text{H}(\text{WO}_5)_3]$ , alkenes and  $\text{H}_2\text{O}_2$  were mixed in solvent, the pre-catalyst reacts with hydrogen peroxide to form another silicon-containing species III that contains the peroxy group. With the increasing of reaction temperature and the aid of long chain of the quaternary ammonium cation, the active silicon-containing species III gradually dissolved in the solvent while the epoxidation reaction took place. The active oxygen in III was transferred to C=C bond of the olefins to afford the epoxide. Once the active oxygen of compound III was losing, it will regenerate again immediately by the oxygen reservoir of the oxidant of hydrogen peroxide in the reaction system. So, the epoxidation catalyzed by III can proceed successively until the use up of oxidant. These soluble species III lost active oxygen and then polymerized into larger silicon-containing species II which was insoluble in ethyl acetate and water at room temperature. Thus, the used catalyst of silicon-containing species II precipitated out from the reaction solution after the hydrogen peroxide was consumed up with the decreasing of reaction temperature. The used catalyst II could be recovered by filtration or centrifugation of the above solid-liquid mixture. The changes of structure for pre-catalyst I and catalyst II



could be clarified by the IR and  $^{29}\text{Si}$  MAS NMR characterization.

For the recycled reactions, firstly, the insoluble catalyst of silicon-containing species II was transferred to the active silicon-containing species III under the action of  $\text{H}_2\text{O}_2$ . Then, a similar epoxidation process as above proceeded. After reaction, the active silicon-containing species III lost its active oxygen and became the silicon-containing species II again, and could be precipitated from the reaction solvent. The used catalyst II was recovered by filtration or centrifugation from the solid-liquid mixture. Therefore this reaction-controlled phase-transfer epoxidation catalyst was recycled many times based on the above reaction mechanism.

Although the silicon-containing species II is the true catalyst, it could not be synthesized directly so far. This case was just as Xi's famous reaction-controlled phase-transfer catalyst  $[\pi\text{-C}_5\text{H}_5\text{N}(\text{CH}_2)_{15}\text{CH}_3]_3[\text{PW}_4\text{O}_{16}]$ , which also acted as precursor for the real catalytic cycles. The recyclable solid catalyst was a mixture of  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ ,  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  and some unidentified heteropolyoxotungstates<sup>23</sup>.



Scheme 2. Reaction mechanism for the epoxidation of olefins with  $\text{H}_2\text{O}_2$  catalyzed by I

### Oxidation of sulfides

The present system also catalyzes the oxidation of various sulfides to sulfoxides and sulfones in reaction-controlled phase-transfer mode. The results are summarized in Table 5. Thioanisole, benzothiophene and dibenzothiophene (Entry 1, 6 and 7) were selectively mono-oxygenated to the corresponding sulfoxides with 100% conversion and 100% yields. For thiophene and its methyl-substituted derivatives, the conversions of substrates were not completed in 2 hours and both sulfoxides and sulfones were produced. Whereas 2,5-dimethylthiophene was selectively mono-oxygenated to the corresponding sulfoxides (ca. 81%) along with formation of the corresponding sulfones (ca. 10%).

The recovery and reuse of the catalyst I was also very efficient, easy and convenient in the oxidation of sulfides. The same phenomena of reaction-controlled phase-transfer catalysis were observed all in these oxidations and excellent

catalytic activity was presented. The recycling experiments over oxidation of thioanisole were shown on Table S2. The yield of methyl(phenyl)sulfane did not drop after five consecutive cycles, a 99% yield of the sulfone was still kept for the oxidation of thioanisole.

Table 5 Oxidation of various sulfides with hydrogen peroxide catalyzed by I.

| Entry          | Substrate | Product 1 | Product 2 | Conversion (%) | Yield 1(%) | Yield 2(%) |
|----------------|-----------|-----------|-----------|----------------|------------|------------|
| 1              |           |           |           | 100            | 0          | 100        |
| 2              |           |           |           | 59             | 35         | 24         |
| 3              |           |           |           | 64             | 58         | 6          |
| 4              |           |           |           | 67             | 45         | 22         |
| 5              |           |           |           | 91             | 81         | 10         |
| 6 <sup>b</sup> |           |           |           | 100            | -          | 100        |
| 7 <sup>c</sup> |           |           |           | 100            | -          | 100        |

<sup>a</sup> Reaction conditions: time 2 h; 2 mL solvent ethyl acetate; 10  $\mu\text{mol}$  (25 mg) cat I; 1 mmol substrate; 2 mmol  $\text{H}_2\text{O}_2$ ; Reaction temperature: 333 K; Yield (%) = products (mol)/ substrate used (mol)  $\times$  100. Conversions and selectivity were determined by gas chromatography using an internal standard technique were based on the substrate. <sup>b</sup> reaction temperature: 343 K, 4 mL solvent ethyl acetate. <sup>c</sup> reaction temperature: 353 K. 4 mL solvent ethyl acetate.

### Oxidation of alcohols

Different kind of alcohols were converted into the corresponding ketones under this reaction-controlled phase transfer catalytic system. The results in Table 6 show that I effectively catalyzes the oxidation of alcohols to

Table 6 Oxidation of various alcohols catalyzed by I with  $\text{H}_2\text{O}_2$ <sup>a</sup>

| Entry | Substrate | Product | Conversion (mol%) | Selectivity (mol%) | Yield (mol%) |
|-------|-----------|---------|-------------------|--------------------|--------------|
| 1     |           |         | 76                | 100                | 76           |
| 2     |           |         | 45                | 100                | 45           |
| 3     |           |         | 48                | 100                | 48           |
| 4     |           |         | 87                | 100                | 87           |

<sup>a</sup> Reaction conditions: 10  $\mu\text{mol}$  catalyst; 2 ml ethyl acetate; 1 mmol substrate; 30% aq.  $\text{H}_2\text{O}_2$  5 mmol; reaction temperature: 353 K, reaction time 10 h; the conversion was based on alcohols, the selectivity was based on ketone, aldehyde or acid.

corresponding carbonyl compounds with hydrogen peroxide. Normal to high conversions and high selectivities for secondary alcohols were observed under our reaction conditions. Especially, the 2-octanol showed a 87% conversion and a 87% yield for octan-2-one.

## Conclusions

In summary, a new reaction-controlled phase-transfer catalyst based on silicotungstate of  $[(C_{18}H_{37})_2(CH_3)_2N]_3[SiO_4H(WO_5)_3]$  (I) was developed. Complex I exhibited high catalytic activity for epoxidation of various alkenes (such as linear terminal olefins, internal olefins, cyclic olefins, styrene, and unactivated alkenes) to epoxides, the oxidation of sulfides and the oxidation of alcohols.

This new reaction-controlled phase-transfer catalytic system not only made the recovery of catalyst easy, but also avoided the using of toxic solvents. All the oxidation reactions were performed in a recyclable and environmentally benign catalytic system:  $[(C_{18}H_{37})_2(CH_3)_2N]_3[SiO_4H(WO_5)_3]/H_2O_2$ /ethyl acetate/substrates. The catalyst was easily recovered after reaction by filtration and centrifugation, and the high activity was maintained for the recycling reactions. It was found that silicotungstate of  $[(C_{18}H_{37})_2(CH_3)_2N]_3[SiO_4H(WO_5)_3]$  (I) was a pre-catalyst and the true catalyst was a mixture that contains several different silicotungstate species.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 21172098, 21173105, 20803032) and the Fundamental Research Funds for the Central Universities (lzujbky-2013-50 and lzujbky-2014-67).

## Notes and references

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 †Electronic Supplementary Information (ESI) available: Experimental details and spectrum characterizations of catalysis reaction. See DOI: 10.1039/c000000x/

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