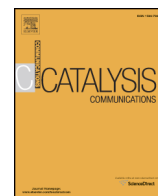




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## Solvent-free Baeyer–Villiger oxidation with H<sub>2</sub>O<sub>2</sub> as oxidant catalyzed by multi-SO<sub>3</sub>H functionalized heteropolyanion-based ionic hybrids

Xinzhong Li<sup>a,b,\*</sup>, Rong Cao<sup>a</sup>, Qi Lin<sup>b</sup><sup>a</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China<sup>b</sup> Department of Chemistry and Chemical Engineering, University of Minjiang, Fuzhou 350108, China

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## ABSTRACT

Three novel multi-SO<sub>3</sub>H functionalized heteropolyanion-based ionic hybrids were synthesized and characterized, which as heterogeneous catalysts for Baeyer–Villiger oxidation using 35% aqueous H<sub>2</sub>O<sub>2</sub> as oxidant show high catalytic activity under solvent-free conditions, the target lactones were obtained with yields of 69% to 88% in 3 h at 50 °C. Three ionic hybrids could be recovered readily and their catalytic activity almost completely retained after ten recycles.

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## 1. Introduction

Baeyer–Villiger oxidation (BV) is one of the most important oxidation reactions in organic chemistry, which provide a simple and efficient approach for converting ketones into the corresponding lactones or esters with excellent region and stereo-selectivity [1]. BV oxidation was widely used in the manufacture of antibiotics, steroids, pheromones and various high valuable fine chemicals [2]. Traditionally, various organic peroxyacids like *m*-chloro-perbenzoic acid, peroxybenzoic acid, and trifluoroperacetic acid are used as oxidants for this transformation, but the use of peroxyacid involves some disadvantages such as expensive, hazardous and dangerous in transportation and storage, large amounts of the corresponding carboxylic acid was formed as wastes, and reactions proceed in halogenated solvent, using a buffer (sodium phosphate etc.) to avoid transesterification, etc. From the atom economy and environmentally friendly point of view, it was pertinent to replace peroxyacids with hydrogen peroxide, which is commercially available, safe and relatively cheap, easy to handle, has a high content of active oxygen and only water was formed as byproduct. However, H<sub>2</sub>O<sub>2</sub> is the weakest oxidant compared to a wide range of available peroxides and peroxyacids, a catalyst is required to increase its nucleophilicity. For this purpose, a number of interesting heterogeneous and homogeneous catalytic systems have been developed, such

as Pt<sup>II</sup>, Sn<sup>IV</sup>, and Sc<sup>III</sup> complexes [3], novel organoborn Lewis acid [4], thiourea-based organic catalysis [5], alkaline earth metal oxide [6], solid acids [7], zeolites [8], Sn-MCM-41 [9], hydrotalcites [10], and Sn-β zeolite [11]. Moreover, ionic liquids and acidic ionic liquids acting as green solvents or both solvents and catalysts also have been applied successfully in the BV oxidations [12–18]. Compared to traditional methods, these reports demonstrated the advantages of reaction carried out at room temperature, high yield and selectivity, short reaction time, simple workup, recyclability of catalyst, using commercially available aqueous H<sub>2</sub>O<sub>2</sub>, etc.

More recently, heteropolyacid-based ionic liquids (HPAILs) as novel functionalized ionic liquids have attracted increasing attentions [19,20]. Which as efficient and recyclable catalysts for lipophilic alkene epoxidation and alcohol selective oxidation with aqueous H<sub>2</sub>O<sub>2</sub> have been reported [21–23]. In order to enhance the acidity of HPAILs, novel SO<sub>3</sub>H-functionalized HPAILs are developed as reaction-induced self separation catalyst in Fischer esterification [24]. But these interesting reports were limited in that only the catalytic activity of heteropolyanion or functionalized organic cation was utilized in the reactions. In addition, these reported HPAILs are solids with high melting point (more than 100 °C), so it is not correct to define them as ionic liquids. Aiming to expand the application of SO<sub>3</sub>H-functionalized HPAILs as green catalysts in organic transformations, we described herein a simple, efficient and eco-friendly approach for BV oxidation with 35% aqueous hydrogen peroxide as oxidant using three multi-SO<sub>3</sub>H functionalized heteropolyanion-based ionic hybrids **S2SiIH**, **S2PIH** and **S4SiIH** (Fig. 1) as heterogeneous catalysts under solvent-free conditions. Under optimum reaction conditions, BV oxidations carried out smoothly and gave the target lactones

\* Corresponding author at: State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China.

E-mail address: [bails\\_wl@126.com](mailto:bails_wl@126.com) (X. Li).

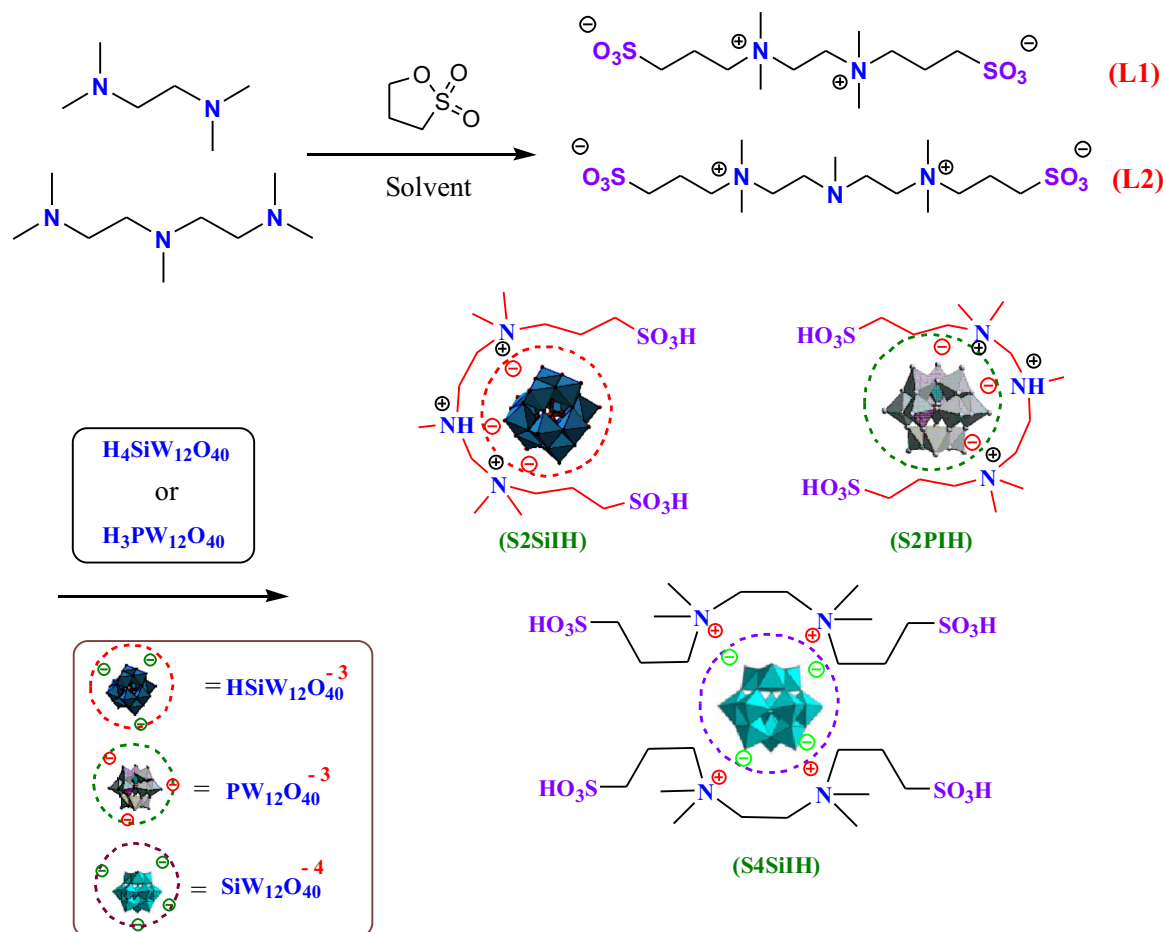


Fig. 1. Synthetic route of long chain SO<sub>3</sub>H functionalized heteropolyanion-based ionic hybrids **S2SiIH**, **S2PIH** and **S4SiIH**.

with yields of 69% to 88%. On completion, three ionic hybrids could be recycled after simple workup and reused for ten times without notable decrease in their catalytic activities.

## 2. Experimental

### 2.1. Materials and methods

All reagents and solvents were used as received. Melting point was determined using an X<sub>4</sub> digital microscopic melting point apparatus with an upper limit of 250 °C. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Burke 400 spectrometer in D<sub>2</sub>O with TMS as internal standard. The C, H, and N elemental analyses were performed on an Elementar Vario EL element analyzer. FT-IR spectra were recorded by a Perkin-Elmer FT-IR 240-c spectrophotometer (KBr pellets). The thermal stability of **S2SiIH**, **S2PIH** and **S4SiIH** was characterized by TGA (Perkin-Elmer TGA instrument, 10 K/min heating rate under N<sub>2</sub> flows). The X-ray diffraction measurements were made on a MiniFlex-600 diffractometer. BET surface areas were measured at the temperature of liquid nitrogen using a Micromeritics ASAP2010 analyzer. The samples were degassed in vacuum at 150 °C for 3 h before measurement. SEM image was performed on a HITACHIS-4800 field emission scanning electron microscope.

### 2.2. Preparations of **S2SiIH**, **S2PIH** and **S4SiIH**

#### 2.2.1. Preparation of **L1** and **L2**

A mixture of *N,N,N',N'*-tetramethylethylenediamine or *N,N,N',N',N''*-pentamethyldiethylenetriamine (1 mol) and 1, 3-propanesultone

(2.1 mol) in CH<sub>3</sub>CN was stirred at room temperature for 48 h. On completion, the formed white crystal were filtered and washed with diethyl ether (3 × 20 mL), then dried under vacuum at 70 °C for 8 h, **L1** and **L2** were obtained with yields of 95% and 97%, respectively.

**L1**: m.p.: 66 °C. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 2.26–2.30 (m, 4H, 2CH<sub>2</sub>), 2.99–3.03 (t, 4H, 2CH<sub>2</sub>), 3.27 (s, 12 H), 3.59–3.64 (t, 4H, 2CH<sub>2</sub>), 3.98 (t, 4H, 2CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O): δ = 31.85 (CH<sub>2</sub>CH<sub>2</sub>N), 47.86 (CH<sub>2</sub>SO<sub>3</sub>), 50.81 (NCH<sub>3</sub>), 63.33 (NCH<sub>2</sub>), 64.17 (CH<sub>2</sub>N). Elemental analysis Calcd for C<sub>12</sub>H<sub>28</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: C, 39.98; H, 7.83; N, 7.77; S, 17.79. Found: C, 39.95; H, 7.81; N, 7.74; S, 17.82.

**L2**: m.p.: 58 °C. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 2.16–2.22 (m, 4H, 2CH<sub>2</sub>), 2.24 (s, 3H, CH<sub>3</sub>), 2.934–2.97 (m, 8H, 4CH<sub>2</sub>), 3.13 (s, 12H, 4CH<sub>3</sub>), 3.47–3.52 (m, 8H, 4CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O): δ = 32.13 (CH<sub>2</sub>CH<sub>2</sub>N), 43.35 (NCH<sub>3</sub>), 48.14 (CH<sub>2</sub>SO<sub>3</sub>), 51.85 ((NCH<sub>3</sub>), 57.64 (NCH<sub>2</sub>), 63.67 (N<sup>+</sup>CH<sub>2</sub>), 64.24 (CH<sub>2</sub>N<sup>+</sup>). Elemental analysis Calcd for C<sub>15</sub>H<sub>35</sub>N<sub>3</sub>O<sub>6</sub>S<sub>2</sub>: 43.14; H, 8.45; N, 10.06; S, 15.95. Found: C, 43.11; H, 8.44; N, 10.01; S, 15.96.

#### 2.2.2. Preparation of **S2SiIH** and **S2PIH**

A mixture of **L2** (1.5 mmol) in 30 mL deionized water was added to an aqueous solution of H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> (1.5 mmol) or H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (1.5 mmol) in drop wise under vigorous stirring, then the resulting mixture was stirred at room temperature for 24. The formed white precipitate was filtered and washed with water (3 × 20 mL), and then dried under vacuum at 80 °C for 8 h, two target ionic hybrids was obtained as off-white powder. **S2SiIH**: yield: 90%. m.p.: >250 °C. BET surface area: 10.71 m<sup>2</sup>/g. FT-IR (KBr, cm<sup>-1</sup>): 3440 ν(N–H), 1190 ν<sub>a</sub>(SO<sub>2</sub>), 1044 ν<sub>s</sub>(SO<sub>2</sub>), 1015 ν(Si–O), 972

$\nu_{\text{as}}(\text{W}=\text{O})$ , 921  $\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W})$ , 792  $\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W})$ , 533  $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$ . Elemental analysis Calcd for  $\text{C}_{14}\text{H}_{36}\text{N}_3\text{SiW}_{12}\text{O}_{46}\text{S}_2$ : C, 5.13; H, 1.10; N, 1.28; S, 1.95. Found: C, 5.11; H, 1.07; N, 1.24; S, 1.88. The decomposition temperature was about 533 K. **S2PIH**: yield: 91%. m.p.: >250 °C. BET surface area: 10.24 m<sup>2</sup>/g. FT-IR (KBr, cm<sup>-1</sup>): 3433  $\nu(\text{N}-\text{H})$ , 2977  $\nu(\text{C}-\text{H})$ , 1200  $\nu_a(\text{SO}_2)$ , 1079  $\nu_{\text{as}}(\text{P}-\text{O})$ , 979  $\nu_{\text{as}}(\text{W}=\text{O})$ , 897  $\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W})$ , 807  $\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W})$ . Elemental analysis Calcd for  $\text{C}_{14}\text{H}_{35}\text{N}_3\text{PW}_{12}\text{O}_{46}\text{S}_2$ : C, 5.12; H, 1.07; N, 1.28; S, 1.95. Found: C, 5.09; H, 1.08; N, 1.26; S, 1.91. The decomposition temperature was about 532 K.

### 2.2.3. Preparation of **S4SiH**

A mixture of **L1** (1.5 mmol) in 20 ml deionized water was added to an aqueous solution of  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  (0.75 mmol) in dropwise within 0.5 h under vigorous stirring, then the resulting mixture stirred at room temperature for 24 h. The formed white precipitate was filtered and washed with water (3 × 20 mL), and then dried under vacuum at 80 °C over 8 h. **S4SiH** was obtained as off-white powder. Yield: 90%. m.p.: >250 °C. BET surface area: 10.53 m<sup>2</sup>/g. FT-IR (KBr, cm<sup>-1</sup>): 3409  $\nu(\text{O}-\text{H})$ , 2977  $\nu(\text{C}-\text{H})$ , 1206  $\nu_a(\text{SO}_2)$ , 1044  $\nu_s(\text{SO}_2)$ , 1014  $\nu(\text{Si}-\text{O})$ , 973  $\nu_{\text{as}}(\text{W}=\text{O})$ , 920  $\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W})$ , 793  $\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W})$ , 533  $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$ . Elemental analysis Calcd for  $\text{C}_{24}\text{H}_{60}\text{N}_4\text{SiW}_{12}\text{O}_{52}\text{S}_4$ : C, 8.00; H, 1.67; N, 1.56; S, 3.56; Found: C, 7.96; H, 1.63; N, 1.52; S, 3.46. The decomposition temperature was about 523 K.

### 2.3. General Procedures of BV oxidation

Ionic hybrid (0.5 mmol) and ketone (10 mmol) was added to a 25 mL flask equipped with a condenser and magnetic stirrer. The reaction was started after the addition of  $\text{H}_2\text{O}_2$  aqueous (35 wt.%, 25 mmol) in dropwise at 50 °C under vigorous stirring. The progress of the reaction was monitored by TLC (hexane/ethyl acetate = 4/1). After the completion, the mixture was extracted with diethyl ether (3 × 15 mL). The combined organic layer was washed with aqueous of  $\text{NaHCO}_3$  (3 × 15 mL) and water (3 × 15 mL), then dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated under vacuum to afford the crude product. The crude product was purified by column chromatography using hexane–ethyl acetate 4:1 (V/V) as eluent. The obtained product was identified by comparing TLC, <sup>1</sup>H NMR and IR spectra data with authentic sample. The catalyst was recovered by washed with diethyl ether (3 × 10 mL), and then dried under vacuum at 80 °C over 8 h. Oxidant efficiency is determined by iodometric titration methods

described in literature [25]. The results revealed that the amount of  $\text{H}_2\text{O}_2$  present at the reaction endpoint was 2–3 mmol.











## 3. Results and discussion

### 3.1. Synthesis of **S2SiH**, **S2PIH** and **S4SiH**

Three ionic hybrids were synthesized using *N,N,N',N'*-tetramethylethylenediamine, *N,N,N',N''*, *N''*-pentamethyldiethylene triamine, 1,3-propanesultone and Keggin type heteropolyacid as starting substrates via quaternization and acidification two step economic reactions. For **S2SiH**, **S2PIH** and **S4SiH**, there are two or four sulfonic acid group functionalized organic cations in their structure together with the counter polyoxometalate anion that not only endowed them with high Brønsted acidity and good oxidation catalytic activity at the same time, but also caused two catalytic activity that can be finely tuned by changing the quantity of sulfonic acid group and choosing different polyoxometalate anion. On the other hand, since heteropolyanion was tightly associated with the counter organic cation by the strong electrostatic interaction, it also realized stable and efficient immobilization for heteropoly acids. Three ionic hybrids were insoluble in water and almost all organic solvents. The content of water in them was measured by Karl–Fischer titration, with the results ranging from 3.2 wt.% to 5.1 wt.%. The obtained TG patterns showed two weight losses, one occurs before 150 °C, this might be ascribed to the lost of crystal water in the counter polyoxometalate anions, these values are roughly agreed with the content of water in them. Further weight loss occurs above 250 °C, this might owe to the decomposition of the organic cations.

In the IR spectra of three ionic hybrids, the characteristic bands for organic cations appeared at 3400, 2900, 1200 and 1044 cm<sup>-1</sup>, which are assigned to the –OH, C–H stretching vibrations and asymmetric and symmetric stretching vibrations of S = O respectively. In the wave-number regions of 750–1100 cm<sup>-1</sup>,  $\text{PW}_{12}\text{O}_{40}^{3-}$  gave four characteristic bands at 1079, 979, 897, and 807 cm<sup>-1</sup>.  $\text{SiW}_{12}\text{O}_{40}^{4-}$  and  $\text{HSiW}_{12}\text{O}_{40}^{3-}$  gave five characteristic bands at 1014, 973, 920, 882, and 793 cm<sup>-1</sup>. These results clearly indicate that the structures of both organic cations and heteropolyanions in **SHPIHS-1–3** are well reserved. The XRD patterns for three ionic hybrids showed that there are no obvious characteristic diffraction peaks of Keggin-type heteropolytungstate that appeared, these results proved that there is no crystalline phase of heteropolytungstate in their structures, which is due to the rearrangement of heteropolyanions with organic cations during the preparation.

**Table 1**  
Results of BV oxidations catalyzed by **S2SiH**, **S2PIH** and **S4SiH**.

Entry	Substrate	Products	Yields (%)	TOF (h <sup>-1</sup> )
1			77 <sup>a</sup> /70 <sup>b</sup> /69 <sup>c</sup>	5.2 <sup>a</sup> /4.6 <sup>b</sup> /4.5 <sup>c</sup>
2			83 <sup>a</sup> /79 <sup>b</sup> /75 <sup>c</sup>	5.6 <sup>a</sup> /5.3 <sup>b</sup> /4.9 <sup>c</sup>
3			88 <sup>a</sup> /82 <sup>b</sup> /80 <sup>c</sup>	2.8 <sup>a</sup> /2.2 <sup>b</sup> /2.0 <sup>c</sup>
4			42 <sup>a</sup> /32 <sup>b</sup> /31 <sup>c</sup>	5.8 <sup>a</sup> /5.5 <sup>b</sup> /5.3 <sup>c</sup>
5			38 <sup>a</sup> /30 <sup>b</sup> /25 <sup>c</sup>	2.5 <sup>a</sup> /2.1 <sup>b</sup> /2.0 <sup>c</sup>

Reaction conditions: temperature 50 °C; time 3 h ketone: $\text{H}_2\text{O}_2$ :ionic hybrids = 1:2.5:0.05 (mol).

<sup>a</sup> Result of **S2SiH**.

<sup>b</sup> Result of **S2PIH**.

<sup>c</sup> Result of **S4SiH**.

The acid contents and acidities of three ionic hybrids were determined by acid base titration and Hammett indicator method according to the methods in literatures [26,27]. The acidity (denoted as Hammett acidities function ( $H_0$ ), Hammett indicator: *p*-nitrotoluene) of **S2SiIH**, **S2PIH** and **S4SiIH** is  $-3.51$ ,  $-3.42$  and  $-3.94$ , respectively. The acid content of **S2SiIH**, **S2PIH** and **S4SiIH** is  $1.12$ ,  $0.98$  and  $1.37$  mmol  $g^{-1}$  respectively. These results indicated that they all exhibited strong Brønsted acidity and high acid content, and these properties are crucial for them as effective catalysts in BV oxidation. Among them, **S4SiIH** exhibit the highest acidity and acid content for its four sulfonic acid groups on organic cation. The reason why **S2SiIH** shows higher acidity and acid content than **S2PIH** lie in its counter anion is  $HSiW_{12}O_{40}^{3-}$ .

### 3.2. BV oxidation catalyzed by **S2SiIH**, **S2PIH** and **S4SiIH**

Initially, the nonstrained cyclohexanone was chosen as a model substrate to investigate the catalytic activity of three ionic hybrids and the effect of catalyst amount, reaction temperature and time. Under optimum conditions, these results are listed in Table 1. Three ionic hybrids all exhibited high catalytic activity for cyclic ketone and aromatic ketone oxidations. For cyclic ketones the corresponding lactones were obtained with yields of 69% to 88%. Based on this success, we continued to carry out the BV oxidation of acyclic ketones, the results are listed in Table 1 (Entries 4–5). For aromatic ketones the corresponding esters are obtained with yields of 25% and 42%, but for aliphatic ketones no corresponding esters were obtained. These results indicated that this approach only has generality for oxidation of cyclic ketones and aromatic ketones. In order to reasonably explain for these good results, the performances of single  $SO_3H$ -functionalized Brønsted acidic ionic liquids **BAILS-1-2** [28] (Fig. 1),  $H_4SiW_{12}O_{40}$ ,  $H_3PW_{12}O_{40}$ , Amberlyst-15 [8] and supported sulfonic acid (silica sulfate) [29] as catalysts in cyclohexanone oxidation under the same reaction conditions were investigated, these results are listed in Table 2. These results indicated that the combining of sulfonic group with heteropoly acid anion is essential for the high catalytic activity. Based on these experimental results, the high catalytic performance of **S2SiIH**, **S2PIH** and **S4SiIH** in BV oxidation could be attributed to the following facts: 1) strong Brønsted acidity and high acid content, which not only enhance the addition activity of carbonyl group on substrate ketones by protonation [30], but also made  $H_2O_2$  to be activated; 2) active persulfonic acid was generated in situ. Three ionic hybrids showed core-shell structure, the outer layer is a multi-sulfonic acid group functionalized organic cations, which was oxidized by the activated  $H_2O_2$ , and generated more active persulfonic acid intermediate; 3) amphiphilic surface. The structure of  $SO_3H$ -functionalized long chain alkylammonium for organic cation endowed three ionic hybrids with excellent amphiphilic surface, which caused the reaction between the ketone and  $H_2O_2$  aqueous to be carried out smoothly; 4) Porous structure. The BET surface areas of **S2SiIH**, **S2PIH** and **S4SiIH** are 10.71, 110.24, and  $10.53$   $m^2$   $g^{-1}$  respectively, though still not high but its catalytic activity for oxidation cyclohexanone is much higher than the **BAILS-1-2**,  $H_4SiW_{12}O_{40}$  and  $H_3PW_{12}O_{40}$  homogeneous catalytic system. These features suggest a bulk-type catalysis mode for three ionic hybrids (not a surface-type), in terms of mass transfer, the ionic hybrid's good catalytic performances are mostly because of the amphiphilic

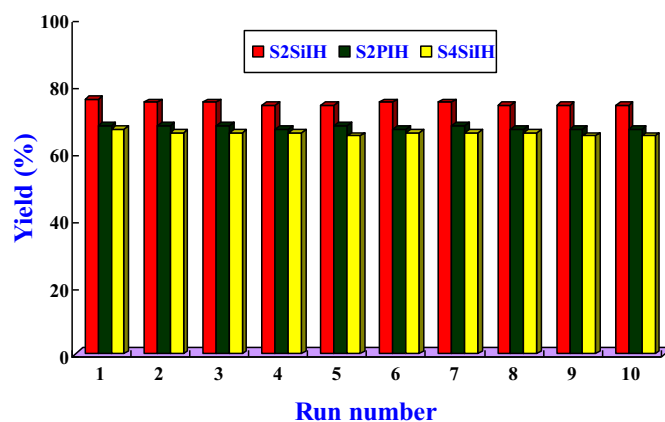


Fig. 2. Recycling of **S2SiIH**, **S2PIH** and **S4SiIH** in the oxidation of cyclohexanone.

environment in bulk areas of the solid hybrid, which are suitable for transportation of both hydrophobic and hydrophilic species; 5) The cooperative catalytic effect of organic cation and heteropolyacid anion. Being polyoxometalate anions, they were enclosed tightly by the counter organic cations, the active persulfonic acid was generated in situ together with the active  $H_2O_2$  that also oxidized them into peroxo intermediate, and two generated active peroxide species together oxidized ketone into the corresponding lactone or ester. With the increasing of sulfonic acid group, the more active peroxide species were obtained, so three ionic hybrids, Amberlyst-15 and silica sulfate gave better results than **BAILS-1-2**,  $H_4SiW_{12}O_{40}$  and  $H_3PW_{12}O_{40}$ . Since oxidation reaction was performed in aqueous solution, with the increasing of acidity and acid content, the hydrolysis rate of obtained lactones increased. Take the conversion and selectivity into account, appropriate acidity and acid content of catalytic system are crucial for the high yield. Compared to **S2PIH** and **S4SiIH**, Amberlyst-15 and  $SiO_2-SO_3H$ , the reason for **S2SiIH** gave the best result that might ascribe to its enough and suitable acidity and acid content.

In order to investigate the recoverability and recyclability of **S2SiIH**, **S2PIH** and **S4SiIH**, the oxidations of cyclohexanone were chosen as model reactions. Three ionic hybrids were regenerated by simple washing with distilled water, diethyl ether and dried at  $85$   $^{\circ}C$  for 8 h. The recycle test results showed that there is only a marginal decrease in yield after they were reused for ten times (Fig. 2). For the purpose of comparison, the TG pattern, IR spectra, acidity and acid content of recycled ionic liquids were also determined, and it has been found that there are no obvious differences between the recycled and fresh samples. These results indicate that three ionic hybrids are stable in the reaction system.

## 4. Conclusion

In conclusion, we have developed a simple, efficient and eco-friendly approach for BV oxidation using three novel multi- $SO_3H$  functionalized **S2SiIH**, **S2PIH** and **S4SiIH** as recyclable catalyst under solvent-free conditions. Several noteworthy features of this approach, including the convenient preparation of three ionic hybrids with high purity and low cost, using commercial available 35% aqueous  $H_2O_2$ , simple workup, high yield, mild reaction conditions, **S2SiIH**, **S2PIH** and **S4SiIH** can be reused after simple treatment, etc. These advantages make this methodology become a green alternative for BV oxidation.

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Table 2

Catalytic performance of various catalysts for BV oxidation of cyclohexanone with  $H_2O_2$ .

Entry	Catalyst	Solubility in reaction	Yields (%)
1	BAILS-1	Soluble	25
2	BAILS-2	Soluble	22
3	$H_3PW_{12}O_{40}$	Soluble	18
4	$H_4SiW_{12}O_{40}$	Soluble	13
5	Amberlyst-15	Insoluble	45
6	$SiO_2-SO_3H^a$	Insoluble	52

Reaction conditions: temperature  $50$   $^{\circ}C$ ; time 3 h ketone: $H_2O_2$ :Cat = 1:2.5:0.05 (mol).

<sup>a</sup>  $SiO_2-SO_3H$  was prepared according to the approach described in literature [29].

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