



Short communication

Solvent-free Baeyer–Villiger oxidation with H₂O₂ as oxidant catalyzed by multi-SO₃H functionalized heteropolyanion-based ionic hybrids

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ABSTRACT

Three novel multi-SO₃H functionalized heteropolyanion-based ionic hybrids were synthesized and characterized, which as heterogeneous catalysts for Baeyer–Villiger oxidation using 35% aqueous H₂O₂ 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, H₂O₂ 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^{II}, Sn^{IV}, and Sc^{III} 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 H₂O₂, 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 H₂O₂ have been reported [21–23]. In order to enhance the acidity of HPAILs, novel SO₃H-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 SO₃H-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-SO₃H 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

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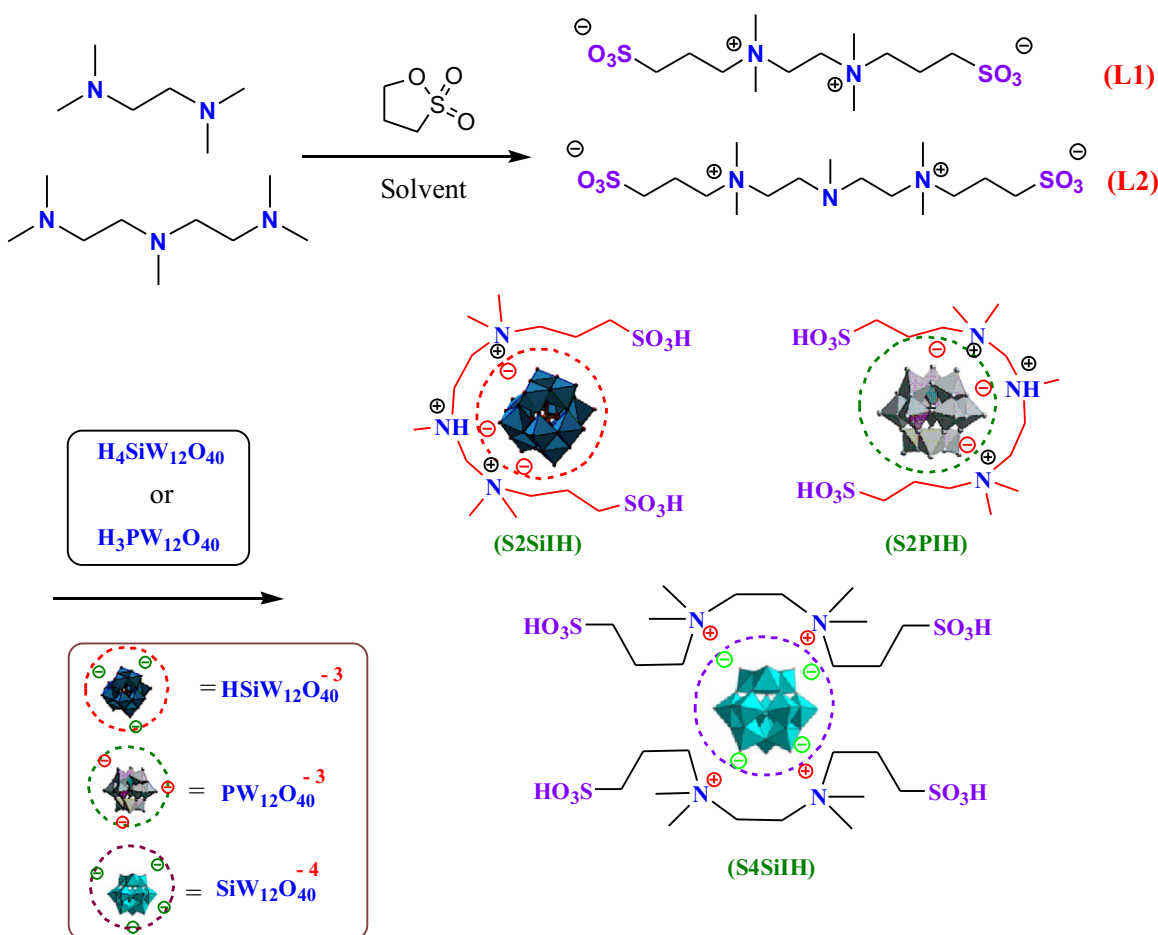


Fig. 1. Synthetic route of long chain SO₃H functionalized heteropolyanion-based ionic hybrids **S2SiIH**, **S2PIH** and **S4SiIH**.

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 X₄ digital microscopic melting point apparatus with an upper limit of 250 °C. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Burke 400 spectrometer in D₂O 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 N₂ 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 CH₃CN 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. ¹H NMR (400 MHz, D₂O): δ = 2.26–2.30 (m, 4H, 2CH₂), 2.99–3.03 (t, 4H, 2CH₂), 3.27 (s, 12 H), 3.59–3.64 (t, 4H, 2CH₂), 3.98 (t, 4H, 2CH₂); ¹³C NMR (100 MHz, D₂O): δ = 31.85 (CH₂CH₂N), 47.86 (CH₂SO₃), 50.81 (NCH₃), 63.33 (NCH₂), 64.17 (CH₂N). Elemental analysis Calcd for C₁₂H₂₈N₂O₆S₂: 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. ¹H NMR (400 MHz, D₂O): δ = 2.16–2.22 (m, 4H, 2CH₂), 2.24 (s, 3H, CH₃), 2.934–2.97 (m, 8H, 4CH₂), 3.13 (s, 12H, 4CH₃), 3.47–3.52 (m, 8H, 4CH₂); ¹³C NMR (100 MHz, D₂O): δ = 32.13 (CH₂CH₂N), 43.35 (NCH₃), 48.14 (CH₂SO₃), 51.85 ((NCH₃), 57.64 (NCH₂), 63.67 (N⁺CH₂), 64.24 (CH₂N⁺). Elemental analysis Calcd for C₁₅H₃₅N₃O₆S₂: 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 H₄SiW₁₂O₄₀ (1.5 mmol) or H₃PW₁₂O₄₀ (1.5 mmol) in drop wise under vigorous stirring, then the resulting mixture was 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 for 8 h, two target ionic hybrids were obtained as off-white powder. **S2SiIH**: yield: 90%. m.p.: >250 °C. BET surface area: 10.71 m²/g. FT-IR (KBr, cm⁻¹): 3440 ν(N–H), 1190 ν_a(SO₂), 1044 ν_s(SO₂), 1015 ν(Si–O), 972

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