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Short communication

Selective oxidation of alcohols with H_2O_2 catalyzed by long chain multi-SO_3H functionalized heteropolyanion-based ionic liquids under solvent-free conditions

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ABSTRACT

Two novel long chain multi-SO_3H functionalized heteropolyanion-based ionic liquids were prepared and characterized. They as homogeneous catalysts showed high catalytic activity in selective oxidation of alcohols with 35% aqueous hydrogen peroxide under solvent-free conditions without adding any phase transfer catalyst. Two ionic liquids can be recovered readily and reused five times without any significant loss in their catalytic activities.

1. Introduction

Oxidation of alcohols to their corresponding carbonyl compounds is one of the most important functional group transformations in organic chemistry and is widely used in academic and industrial processes [1]. Traditionally, this transformation was carried out using stoichiometric inorganic oxidants (i.e. CrO_3, $KMnO_4$, NaClO, MnO_2, PCC, etc.) in the liquid phase [2]. However, these oxidants are toxic, hazardous to handle, expensive, and lack of selectivity and large amounts of wastes are generated [3]. From the atom economy and environmentally friendly point of view, the development of clean and green approaches utilizing H_2O_2 or molecular oxygen as oxidant in combination with recyclable catalysts has attracted increasing attention [4,5], and a lot of novel and efficient homogeneous and heterogeneous catalysts have been reported, such as organometallic complexes [6–10], polyoxometalates [11], supported heteropolyacids [12], heteropolyacid hybrids [13–16], noble metal nanoparticles [17,18], supported Pd [19], and mesoporous oxovanadium Schiff base complex [20].

Recently, novel heteropolyacid-based ionic liquids (HPAILs) as green heterogeneous catalysts showed excellent catalytic performances in selective oxidation of benzyl alcohol with aqueous H_2O_2 [21,22]. However, these reports suffer from using organic solvents, low efficiency of H_2O_2 utilization, mass transfer limitation, lack of generality, etc. In addition, the used HPAILs are solid at room temperature with high melting point over 100 °C, so defining them as ionic liquids is wrong.

Herein, we report a facile and efficient approach for selective oxidation of alcohols catalyzed by two long chain multi-SO_3H functionalized heteropolyanion-based ionic liquids (Scheme 1) with 35% aqueous H_2O_2 under solvent-free conditions without adding any phase transfer catalyst. The corresponding aldehydes and ketones were obtained with yields of 63%–100%. For benzyl alcohols, the corresponding benzoic acids were obtained with yields of 64%–94%. After the completion, two ionic liquids can be reused five times after simple removal of water and without significant loss of their catalytic activities.

2. Experimental

2.1. Materials and methods

Melting points were determined by an X_6 digital microscope melting point apparatus. FT-IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using liquid film. ^1H NMR spectra were recorded on a Bruker Avance-DRX-400 spectrometer using TMS as internal standard. The elemental analyses were performed on an Elementar Vario EL III analyzer. TG analysis was carried out with a STA-409 instrument in dry air flow at a heating rate of 10 °C/min. All chemicals were commercially available and used as received.

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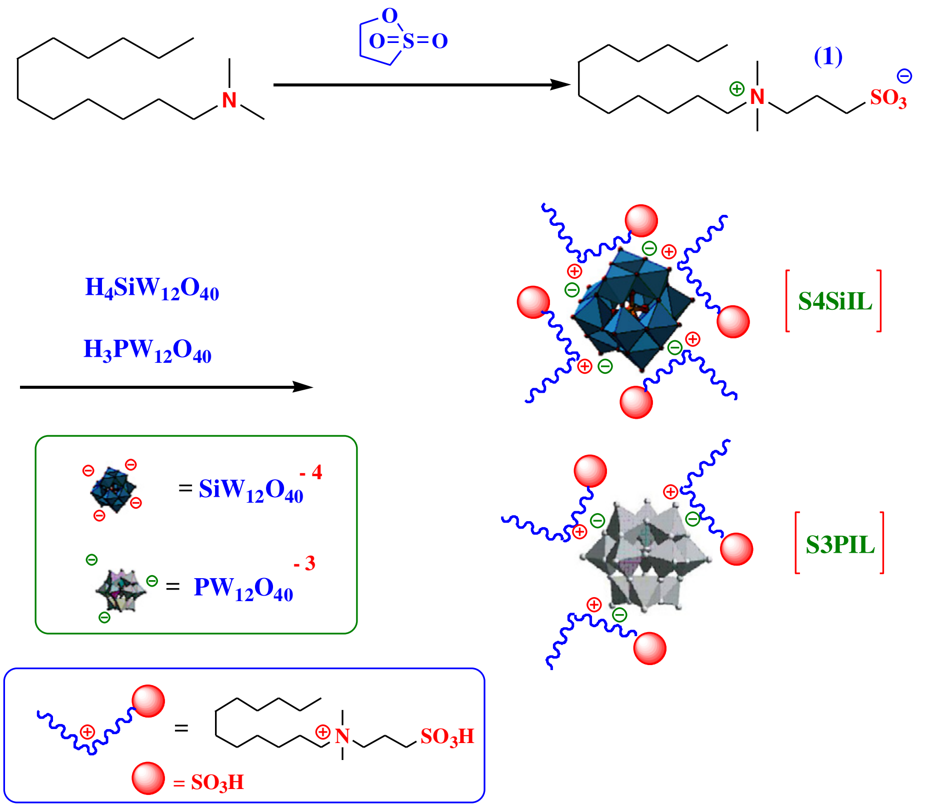

Scheme 1. Synthetic route and structures of **S4SiIL** and **S3PIL**.

2.2. Preparations of S4SiIL and S3PIL

A mixture of *N*, *N*-dimethyldodecylamine (50 mmol) and 1, 3-propanesultone (52 mmol) in ethanol (20 mL) was stirred at room temperature for 24 h. On completion, this reaction system was placed in an ice-water bath and cooled to 0–5 °C, the resulting precipitate was filtered, washed with diethyl ether, and dried at 65 °C under a vacuum for 8 h to afford precursor zwitterionic salt (**1**) in a yield of 95%. After the obtained zwitterionic salt was dissolved in ethanol, $H_4SiW_{12}O_{40}$ (12.5 mmol) or $H_3PW_{12}O_{40}$ (16.7 mmol) aqueous solution was added dropwise, the resulting mixture was stirred at 40 °C in an oil batch for 24 h. After removal of ethanol and water under vacuum, **S4SiIL** and **S3PIL** were obtained as off-white viscous liquids at room temperature with yields of 97% and 98%, respectively.

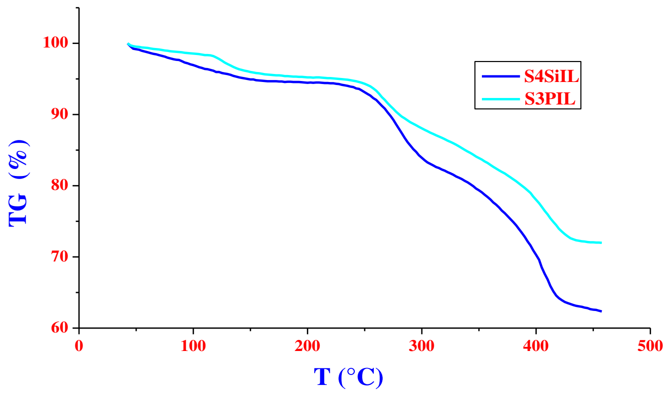

Fig. 1. TG patterns of **S4SiIL** and **S3PIL**.

2.2.1. Compound 1 [23]

Off-white crystal. m.p: 249–252 °C.^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 0.848 (t, $J = 7.2$Hz, 3H, CH_3), 1.262–1.337 (m, 18H, $9CH_2$), 1.725 (m, 2H, CH_2), 2.141–2.200 (m, 2H, CH_2). 2.918 (t, $J = 7.2$Hz, 2H, CH_2), 3.085 (s, 6H, CH_3), 3.281 (m, 2H, CH_2), 3.428–3.470 (m, 2H, CH_2). Elemental analysis Calcd for C_{17} $H_{37}O_3S$: C, 80.55; H, 4.69; N, 9.39; S, 12.65. Found: C, 80.60; H, 4.72; N, 9.43; S, 12.57.

2.2.2. S4SiIL

^{1}H NMR (400 MHz, $CDCl_3$): the values of δ are identical to those of compound **1**. FT-IR, cm^{-1}: 3415, 2924, 1170, 1042, 1013, 974, 919, 883, 796. Elemental analysis Calcd for $C_{68}H_{152}N_3O_{52}S_4SiW_{12}$: C, 19.36; H, 3.63; N, 1.33; S, 3.04. Found: C, 19.32; H, 3.60; N, 1.28; S, 2.97.

2.2.3. S3PIL

^{1}H NMR (400 MHz, $CDCl_3$): the values of δ are identical to those of compound **1**. FT-IR, cm^{-1}: 3400, 2924, 1467, 1079, 1048, 978, 896, 818. Elemental analysis Calcd for $C_{51}H_{144}N_3O_{49}S_3PW_{12}$: C,15.64; H, 3.71; N, 1.07; S, 2.46. Found: C, 15.60; H, 3.68; N, 1.04; S, 2.40.

Table 1
Hammett acidity function of **S4SiIL** and **S3PIL**.

Ionic liquids	Con. (mol/L)	Amax	[B]/%	$[BH^+]$/%	H_0	H_0^1
S4SiIL	0.016	0.978	57.00	42.50	1.121	1.557
S3PIL	0.016	1.045	61.43	38.56	1.192	1.557
S4SiIL	0.032	0.953	56.30	43.97	1.095	1.211
S3PIL	0.032	0.976	57.38	42.62	1.119	1.211
S4SiIL	0.048	0.928	54.56	45.44	1.069	1.112
S3PIL	0.048	0.968	56.91	43.09	1.111	1.112
S4SiIL	0.064	0.916	53.85	46.15	1.057	1.095
S3PIL	0.064	0.926	54.44	45.56	1.067	1.095

$H_0 = PKa + \log[B]/[BH^+]$; indicator: 4-nitroaniline; $PKa = 0.99$; H_0^1: Hammett function of H_2SO_4.