



Heteropolyanion-based sulfated ionic liquid catalyzed formamides synthesis by grindstone chemistry



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ABSTRACT

A novel heteropolyanion-based sulfated ionic liquid (HIL-[Ch-OSO₃H]₃W₁₂PO₄₀) was prepared by pairing sulfate functionalized cholinium cation [*N,N,N*-trimethyl-2-(sulfoxy)ethanaminium] with catalytically active phosphotungstic acid anion (W₁₂PO₄₀³⁻). It was characterized by ¹H NMR, FT-IR, EDX, XRD, TGA and elemental analysis. Catalytic activity of thus prepared HIL was studied in *N*-formylation of amines under solvent-free grinding condition. The methodology provided cleaner conversion over shorter reaction time with high turnover frequency (TOF) and chemoselectivity.

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1. Introduction

Increasing awareness in catalytic synthetic methods for organic motifs in commercial processes is of current interest. Convenient and rapid synthetic procedures are highly desirable which are energy efficient. Reactions under solvent-free conditions have also gained much popularity [1,2]. The simple mechanochemical method, grinding with pestle and mortar, has been claimed to be such a powerful technique [3–8]. A variety of reactions such as homocoupling of terminal alkynes [9], Sonogashira [10], aldol reactions [11] and some other reactions [12,13] have been performed very competently by this technique. However, the technique has remained rather poorly understood and its scope is barely explored.

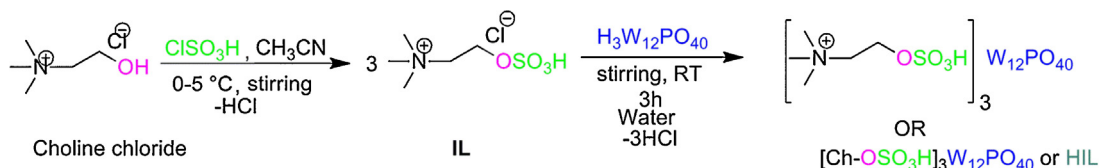
Heteropolyacids (HPAs) and their salts have been widely investigated as solid acid catalysts [14]. Ionic liquids (ILs) have attracted interest as the environmentally friendly solvents with multiple applications in synthesis and catalysis [15–17]. The combination of cation with heteropolyanions can cause the formation of HPA salts, novel type of ILs, which have been employed as the catalysts [18–21]. A large variety of such task specific ILs has been reported in which functional groups are bound to their cations or anions [22–26]. Choline chloride, a biocompatible quaternary ammonium salt, has unique properties such as inexpensive, non-toxic, environmentally benign and non-flammable [27]. Choline

based catalysts showed significant activity in organic syntheses [28–30]. In the present study choline chloride has been attempted to prepare a novel heteropolyanion-based sulfated ionic liquid (HIL-[Ch-OSO₃H]₃W₁₂PO₄₀). It is reported for the first time by pairing sulfate functionalized cholinium cation [*N,N,N*-trimethyl-2-(sulfoxy) ethanaminium] with catalytically active phosphotungstic acid anion (W₁₂PO₄₀³⁻).

Formylation of amines is an important process in organic synthesis with the resulting formamide function being a crossroad intermediate. They are important precursors for synthesis of isocyanides [31,32], formamidines [33], oxazolidinones [34], in the Vilsmeier reaction [35], catalyst for allylation and hydrosilylation of carbonyls [36,37] and also as an important amino protecting group in peptide synthesis [38]. The reaction of amines with formic acid was first reported in 1955 by Fieser and Jones [39]. Since then, several approaches have been reported for *N*-formylation of amines [40–51]. Many of these methods suffer from drawbacks such as expensive reagents, long reaction time, high reaction temperature, thermal instability of catalyst and the extensive use of solvents.

In continuation of our previous efforts for environmentally benign protocols for various organic transformations [15,52–57], we herein first time report a convenient, eco-friendly procedure using an inexpensive and reusable green heterogeneous catalyst for *N*-formylation of amines. In the present report, we have focused on the synthesis of molten salts by pairing of sulfate functionalized cholinium cations with phosphotungstic acid anion, its characterization and catalytic applications in formylation of amines. It was demonstrated that the catalyst was very active, possessed high

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Scheme 1. Synthesis of sulfated functionalized choline chloride (IL) and (HIL).

turnover frequency (TOF) and showed chemoselectivity for the solvent-free formylation of amines.

2. Experimental

2.1. Materials and instrumentation

All the reactions were performed with commercially available reagents. The reactions were monitored by thin-layer chromatography carried out on fluorescent coated plates (aluminium plates coated with silica gel 60 F254, 0.25 mm thickness, Merck) and detection of the components was made by exposure to UV light. The synthesized compounds were characterized by ^1H NMR spectra recorded in DMSO on Bruker Avance 400 MHz spectrometer (Bruker Scientific Corporation Ltd., Switzerland). IR spectra were recorded on Bruker 10 alpha E-FTIR spectrophotometer in the range 4000–400 cm^{-1} . IR frequencies of only characteristic peaks are expressed in cm^{-1} . X-Ray powder diffraction (XRD) patterns were measured on a Philips X-pert MPD using Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) in the range of 2θ 10–70°. The powdered samples were pressed to pellets and fixed to a stainless steel sample holder without further treatment. The EDX was performed using Philips XL 30 scanning electron microscope (SEM). Elemental analyses were performed on PerkinElmer 2400 series-II elemental analyzer (PerkinElmer, USA). Elements were found within $\pm 0.4\%$ of the theoretical compositions for all samples. TGA data was obtained on a TGA/DTG analyzer (TA instruments model 5000/2960 thermo gravimetric analyzer, USA) at a heating rate of 10 $^\circ\text{C}/\text{min}$ under static air atmosphere.

2.2. Catalyst preparation

2.2.1. Preparation of sulfate functionalized cholinium cation (ionic liquid-IL)

To a magnetically stirred mixture of choline chloride (0.02 mol, 2.79 g) in 20 mL of acetonitrile, chlorosulfonic acid (0.02 mol, 1.33 mL) was added dropwise maintaining the temperature below 5 $^\circ\text{C}$ over a period of 2 h (Scheme 1). HCl gas, immediately liberated from the reaction vessel, was properly trapped. After complete addition, the mixture was stirred for further 2 h at room temperature ($27 \pm 1 \text{ }^\circ\text{C}$). The mixture was then filtered, obtained solid was washed with 30 mL of acetonitrile and dried at room temperature to afford *N,N,N*-trimethyl-2-(sulfoxy)ethanaminium chloride (IL).

2.3. Spectral data of *N,N,N*-trimethyl-2-(sulfoxy)ethanaminium chloride (IL)

^1H NMR: ^1H NMR (400 MHz, D_2O): δ (ppm) 3.09 (s, 9H), 3.40–3.42 (m, 2H), 3.93–3.97 (m, 2H); ^{13}C NMR (100 MHz, D_2O): δ (ppm) 53.8 (CH_3), 53.8 (CH_3), 53.9 (CH_3), 67.4 (CH_2), 67.4 (CH_2); ESIMS, m/z : 185.12 (M + 1).

2.3.1. Preparation of HIL

Under vigorous stirring the aqueous solution of *N,N,N*-trimethyl-2-(sulfoxy)ethanaminium chloride (IL, 0.015 mol, 3.30 g) in 25 mL of deionized water was added dropwise into

the aqueous solution of $\text{H}_3\text{W}_{12}\text{PO}_{40}$ (0.005 mol, 14.40 g) at room temperature ($27 \pm 1 \text{ }^\circ\text{C}$) under nitrogen atmosphere (Scheme 1). The product $[\text{Ch-OSO}_3\text{H}]_3\text{W}_{12}\text{PO}_{40}$ (HIL), in the form of white solid was immediately precipitated from the solution. The mixture was stirred at room temperature ($27 \pm 1 \text{ }^\circ\text{C}$) for further 3 h. Solid product was then filtered, washed with deionized water and dried in an oven at 60 $^\circ\text{C}$. It was characterized by FT-IR, XRD, EDX, TGA and elemental analysis.

2.4. Experimental procedures for *N*-formylation of amines

2.4.1. *N*-formylation of primary amines using HIL by grindstone chemistry

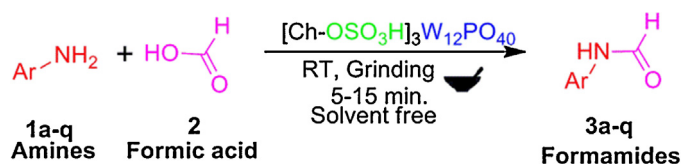
A mixture of amine (1 mmol), aq. formic acid (98%, 3 mmol, 0.11 mL) and 20 mg of HIL was thoroughly mixed in a mortar followed by grinding at room temperature ($27 \pm 1 \text{ }^\circ\text{C}$) (Scheme 2). The syrupy mixture got solidified within 5–15 min. The mixture was pulverized till the completion of reaction as indicated by TLC (Table 4). The reaction mass was then dissolved in ethanol to recover the insoluble catalyst. The filtered catalyst was dried at 80 $^\circ\text{C}$ under vacuum for 2 h after thorough washing with ethanol. Recovered HIL was recycled in the model reaction for six times to check its catalytic efficiency. The products were recrystallized from hot ethanol. The structures of the products were confirmed by ^1H NMR, IR spectroscopy and elemental analysis. The spectral data for all compounds is in good agreement with the reported compounds.

2.5. Selected spectral data of synthesized compounds

N-phenylformamide(3a). Yield: 99%, ^1H NMR (400 MHz, DMSO): δ (ppm) 10.17 (brs, 1H), 8.80 (d , $J = 11.20 \text{ Hz}$, *trans*, 1H), 8.28 (brs, 1H, *cis*), 7.81 (d , $J = 7.56 \text{ Hz}$, 1H, *cis*), 7.05–7.60 (m, 5H, Ar-H); IR (KBr): 3266, 3067, 2760, 1680, 1601, 1543, 1441, 1308, 1148 cm^{-1} ; Anal. Calcd. $\text{C}_7\text{H}_7\text{NO}$ (121.1): C, 69.41%; H, 5.82%; N, 11.56%; Found: C, 69.50%; H, 5.89%; N, 11.52%.

N-(4-chlorophenyl)formamide(3e). Yield: 98%, ^1H NMR (400 MHz, DMSO): δ (ppm) 10.31 (brs, 1H), 8.79 (d , $J = 11.20 \text{ Hz}$, *trans*, 1H), 8.29 (brs, 1H, *cis*), 7.20–7.64 (m, 4H, Ar-H); IR (KBr): 3242, 3052, 2750, 1680, 1601, 1543, 1441, 1308, 1148, 723 cm^{-1} ; Anal. Calcd. $\text{C}_7\text{H}_6\text{ClNO}$ (155.6): C, 54.04%; H, 3.89%; N, 9.00%; Found: C, 54.23%; H, 3.75%; N, 9.08%.

N-(3-hydroxyphenyl)formamide(3p). Yield: 95%, ^1H NMR (400 MHz, DMSO) δ 10.04 (brs, 1H, *trans*), 9.51 (s, 1H, OH), 8.73 (d , 1H, $J = 10.8 \text{ Hz}$, *trans*), 8.23 (s, 1H, *cis*), 6.50 (d , $J = 8.8 \text{ Hz}$, 1H, *cis*) 6.57–7.19 (m, 4H, Ar-H); IR (KBr): 3458, 3284, 2769, 1710, 1589, 1451, 1140 cm^{-1} ; Anal. Calcd. $\text{C}_7\text{H}_7\text{NO}_2$ (137.1): C, 61.31%; H, 5.14%; N, 10.21%; Found: C, 61.52%; H, 5.04%; N, 10.15%.



Scheme 2. Chemoselective *N*-formylation of amines.

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