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Novel SO₃H-functionalized polyoxometalate-based ionic liquids as highly efficient catalysts for esterification reaction

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Abstract

Three novel heteropolyanion-based Brønsted acidic ionic liquids (BAILs), butane mono sulfoacid-functionalized 1,10-phenanthrolinum, butane mono and bis sulfoacid-functionalized 1,4dimethylpiperazinium salts of phosphortungstate catalyst (PhBs₁-PW, [PipBs₁]₃-PW and [PipBs₂]₃-(PW)₂) were synthesized and well characterized with FTIR, ¹H and ¹³C NMR, Electro-Spray Ionization Mass Spectrometry (ESI-MS), Elemental analysis (CHNS), EDX and TG analysis techniques. The esterification reactions of monocarboxylic acids with monohydric alcohols were carried out using these catalysts. The introduced catalysts present a self-separation performance after reaction, which can be easily recovered and quite steadily reused as confirmed by six-run recycling test. Moreover, bis sulfoacid-functionalized 1,4-dimethylpiperazinium salt of phosphortungstate showed the best catalytic performance among the prepared catalysts for the esterification reaction.



Keywords: 1,10-Phenanthroline; 1,4-dimethylpiperazine; 1,4-Butane Sultone; Heteropoly Acid; Ionic Liquid Catalyst; Reusable Catalyst; Esterification Reaction.

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1. Introduction

Since the past decade, ionic liquids (ILs) have received much attention as effective and eco-friendly reaction media due to their unique properties such as negligible vapor pressure, good thermal stability, high ion conductivity, simple functionality and ease of recovery/reuse processes [1,2]. Nevertheless of their environmental compatibility, the role of ILs as solvent almost is not cost-effective and not entirely satisfactory in most cases because the present systems still suffer from high content of ILs (20–300 mol%) needed as the reaction media, relatively long reaction time, and the need to remove by-product from the IL phase in the IL recycling experiment. For this reason, a new window at the ILs was opened with targeted applications. The term "task-specific IL" refers to the non-solvent applications of the ILs such as catalyst in the organic synthesis [3–5]. Probably, the most significant subcategory of the task-specific ILs is referred to as BAIL. High thermal stability, high acidity accompanied by a negligible release of hazardous gases, simple separation and reusability for several times are among the advantages of the BAIL [6,7].

Heteropolyacids (HPAs) are complex protic acids with self-specific structural and physicochemical properties [8–11]. HPAs are highly soluble in polar solvents and ultra-strong Brønsted acidity welcomes them to the solid superacids classification [12,13]. The investigations have showed that in HOAc solution, HPAs act like monobasic acids due to the low degree of dissociation [14].

HPAs have versatile properties such as strong acidity, good thermal stability, and excellent oxidizing capability. These together with the stable and relatively nontoxic characteristics rendering HPA widely appreciated as environmentally benign catalysts for practical replacement of hazardous conventional liquid acids used in industrial processes. However, the unmodified HPAs as catalysts suffer from several disadvantages, such as poor solubility, low selectivity and difficulty in recovery. Moreover, in non-polar medium, the HPAs are not soluble and marginally active due to low accessibility to their active sites. Furthermore, bulk HPAs are soluble in polar media that leads in difficulty of their recovery. It has been found that when HPAs are immobilized on suitable supports with large surface area, the catalytic activity of well-dispersed HPAs could be improved and simple separation of the supported catalysts from the reaction media and products would be easily accessible [15,16].

Unfortunately, the use of supported HPA catalysts is not recommended in polar solvents (e.g., H_2O or HOAc), because of their high solubility in these solvents which in turn leads to leaching of HPA from the solid support and compromises the above mentioned advantages of the supported HPA catalyst. Thus, to facilitate easy separation of the products or recovery and recycling of the HPA catalyst, an innovative design of a homogeneous catalyst would be desirable.

To rich this goal, a new family of BAIL, which was composed of POM polyoxometalate () anions and appropriate organic cations, has attracted intense interest. BAILs-cation salts of HPAs usually have high melting points due to the large volume and high valence of HPA-anions[17]. Up to now, a series of novel HPA-IL catalysts have been prepared and their catalytic activities have been investigated in various organic transformations [18-24].

Herein, we wish to develop the preparation, characterization and investigation the catalytic activity of a new series of ILs-cation phosphotungstate based on 1,4-dimethyl piperazine and 1,10-phenantroline for the esterification reaction.

2 Experimental

All materials were purchased commercially from Fluka Chemical Corp. and Merck & Co., Inc. and were used without further purification. ¹H NMR spectra of samples were recorded at a Bruker Advanced DPX 400-MHz spectrometer. Fourier transform infrared (FT-IR) spectra were obtained as potassium bromide pellets in the range400–4000 cm⁻¹ using an AVATAR 370 Thermo Nicolet spectrophotometer. Thermogravimetric analyses (TGA) were performed using a Du Pont 2000 thermal analysis apparatus at heating rate 5° C min⁻¹ from 30 to 800° C under air atmosphere. The sample weight was *ca*. 10 mg and was heated from room temperature up to 600° C with 10° C/min using alumina sample holders.

2.1.1 Preparation of 4-(1,10-phenanthrolin-1-ium-1-yl)butane-1-sulfonate (PhBs₁)

1,10-Phenanthroline (10 mmol) and 1,4-butane sultone (20 mmol) were dissolved in anhydrous toluene (10 mL), with a stirring at 75 °C for 24 h under nitrogen atmosphere. The resulting white precipitate (PhBs₁) was filtered and washed with diethyl ether and then dried in vacuum (Scheme 1, **1a**). A 87% yield of white solid product was obtained. (ESI-MS) m/z Calcd for PhBs₁: 316.37; Found: 316.08. Anal. Calcd for $C_{16}H_{16}N_2O_3S$ (316.37): C, 60.74; H, 5.09; N, 8.86. Found: C, 60.79; H 5.1; N, 8.91%.

The spectral data for PhBs₁: ¹H NMR (400 MHz, DMSO, TMS): δ 1.16 (quintet, 2H, *J* = 7.6 Hz), 2.16 (quintet, 2H, *J* = 7.6 Hz), 2.46 (t, 2H, *J* = 7.6 Hz), 5.96 (t, 2H, *J* = 7.6 Hz), 8.1 (m, 1H), 8.40-847 (m, 3H), 8.82 (m, 1H), 9.34 (m, 1H), 9.41 (m, 1H), 9.66 (m, 1H). ¹³C NMR (400 MHz, DMSO): δ 22.4, 27.7, 50.7, 51.9, 56.8, 121.1, 121.3, 124.2, 128.1, 128.4, 128.8, 136.3, 138.2, 143.2, 146.9, 150.2, 199.1. 2.1.2 Preparation of 4-(1,4-dimethylpiperazin-1-ium-1-yl)butane-1-sulfonate (PipBs₁)

A round bottom flask containing a magnet was charged with 1,4-dimethylpiperazine (10 mmol) and 1,4-butane sultone (15 mmol) and stirred for 4 h under nitrogen atmosphere at room temperature. The resulting white precipitate was filtered and washed with diethyl ether and then dried in vacuum which was named as $PipBs_1$ (Scheme 2, **2a**). A 95% yield of white solid product was obtained.

The spectral data for PipBs₁: ¹H NMR (400 MHz, D₂O, TMS): δ 1.65-1.80 (m, 2H), 1.81-1.97 (m, 2H), 2.28 (s, 3H), 2.66-2.86 (m, 4H), 2.88 (t, 3H, *J*= 6.8 Hz), 3.02 (s, 3H), 3.20-3.50 (m, 6 H). ¹³C NMR (400 MHz, D₂O): δ 20.3, 22.1, 31.20, 46.7, 50.5, 54.0, 56.5, 58.1. Anal. Calcd for C₁₀H₂₂N₂O₃S: C, 47.98; H, 8.86; N, 11.19; S, 12.81. Found: 47.95; H, 8.90; N, 11.21; S, 12.83.

2.1.3 Preparation of 1,4-dimethylpiperazine-1,4-diium-1,4-diyl)bis(butane-1-sulfonate) (PipBs₂)

A round bottom flask containing a magnet was charged with 1,4-dimethylpiperazine (10 mmol) and 1,4-butane sultone (30 mmol) and stirred for 2h under nitrogen atmosphere at 60 °C. The resulting white precipitate was filtered and washed with diethyl ether and then dried in vacuum which was named as $PipBs_2$ (Scheme 2, **2b**). A 90% yield of white solid product was obtained.

The spectral data for PipBs₂: ¹H NMR (400 MHz, D₂O, TMS): δ 1.65-1.82 (m, 4H), 1.82-2.35 (m, 4H), 2.90 (t, 4H, *J*= 8 Hz), 3.22 (s, 3H), 2.24 (s, 3H), 3.30-4.50 (m, 12H). (ESI-MS) m/z Calcd for PipBs₂: 386.15; Found: 306.12. Anal. Calcd for C₁₄H₃₀N₂O₆S₂: C, 43.50; H, 7.82; N, 7.25; S, 16.59%. Found: C, 43.40; H, 7.88; N, 7.23; S, 16.63%

2.2 Preparation of the $[PhBs_1]^+_{3}PW_{12}O_{40}^{3-}$, $[PipBs_1]^+_{3}PW_{12}O_{40}^{3-}$ and $[PipBs_2]^{2+}_{3}(PW_{12}O_{40}^{3-})_2$ catalysts

PhBs₁ (18 mmol) or PipBs₁ was dissolved in 25 ml of distillated water and added to a round bottom flask containing a magnet and 25 ml of an aqueous solution of $H_3PW_{12}O_{40}$ (6 mmol). Then, the mixture was stirred at room temperature for 24 h. Finally, water was removed in vacuum to give $[PhBs_1]^+_3PW_{12}O_{40}^{3-}$ or $[PipBs_1]^+_3PW_{12}O_{40}^{3-}$ as solids. For the preparation of $[PipBs_2]^{2+}_3(PW_{12}O_{40}^{3-})_2$ catalyst 12 mmol of $H_3PW_{12}O_{40}$ and 18 mmol of PipBs₂ were used with the same procedure. To simplify the catalyst names we used $[PhBs_1]_3$ -PW (1c), $[PipBs_1]_3$ -PW (2c) and $[PipBs_2]_3$ -(PW)₂ (2d) in the text. The acid strength of the salts was measured with Hammett indicators (-3.0 < H_0 < 0.8), including crystal violet (pKa = 0.8), dicinnamalacetone (pKa = -3.0), and anthraquinone (pKa = -8.20). The prepared catalysts were characterized with FT-IR, ¹HNMR, ¹³CNMR, TG and EDX analysis.

The spectral data for $[PhBs_1]^+_{3}PW_{12}O_{40}^{3-}$ (**1c**): FTIR (KBr): 3428.8, 3074, 2925.5, 1629.5, 1527.3, 1467.5, 1434.8, 1351.8, 1230.3, 1153.2, 1078, 1035.6, 977.7, 894.8, 809.9, 715.4, 593.9, 511. Positive-ion electro-spray ionization mass spectrometry: (ESI-MS) m/z calc. 316.09, found. 316.2 (PhBs₁⁺). Negative-ion electro-spray ionization mass spectrometry: (ESI-MS) m/z calc. 959.1, found. 959.5 (PW₁₂O₄₀³⁻).

The spectral data (FTIR (KBr) for $[PipBs_1]_{3}^{+}PW_{12}O_{40}^{3-}$ (**2c**) and $[PipBs_2]_{3}^{2+}(PW_{12}O_{40}^{3-})_2$ (**2d**) catalysts: FTIR (KBr) for $[PipBs_1]_{3}^{+}PW_{12}O_{40}^{3-}$: 1507, 1217, 1079, 1039, 977, 895, 801, 508 cm⁻¹. FTIR (KBr) for $[PipBs_2]_{3}^{2+}(PW_{12}O_{40}^{3-})_2$: 1473, 1217, 1079, 977, 895, 802, 517 cm⁻¹. 2.3 Typical procedure for the [PhBs₁]₃-PW, [PipBs₁]₃-PW and [PipBs₂]₃-(PW)₂ catalyzed esterification reaction

In a typical esterification reaction procedure, a round-bottomed flask with a water segregator was charged with acetic acid (1.80 g, 30 mmol), n-butanol (2.67 g, 36 mmol), and optimized amount of each catalyst (0.25 g of [PhBs₁]₃-PW, 0.25 g of [PipBs₁]₃-PW and 0.15 g of [PipBs₂]₃-(PW)₂). The resulting solution was heated under reflux condition at 110 °C for 1.5 h with vigorous stirring, see Scheme 3. Then, the reaction mixture was cooled to room temperature. The top liquid layer was simply separated by decantation (or filtration) and analyzed using the gas chromatography. For other esterification reactions, the test was carried out accordingly. Exceptionally, for esterification of acetic acid with ethanol, cyclohexane was added as the water-carrying agent.

3. Results and Discussion

3.1 Preparation of [PhBs₁]₃-PW (1c), [PipBs₁]₃-PW (2c) and [PipBs₂]₃-(PW)₂ (2d) catalysts

The representation routes followed to prepare the novel introduced BAILs-PW are depicted in scheme 1 and 2. At the first, in a clean simple two steps procedure [PhBs₁]₃-PW (Scheme 1, 1c) catalyst was obtained (Scheme 1). Typically, 1,10-phenanthroline and 1,4-butane sultone were mixed and heated in dry toluene. After completion of the prcipitation, the mixture was filtered and the white pricipitate was washed sereval times with acetone and dried which was named as Phenanthrolinum-Butane sulfonate (PhBs₁). Then, PhBs₁ was added to an aquas solution of H₃PW₁₂O₄₀ and stirred for 24 h. Finally, water was evaporated under vacuum to give [PhBs₁]₃-PW which was completly soluble in water and was insoluble or very low soluble in aprotic solvents. It is worth to note that the attempts to graft two sulfonate linker to 1,10-phenanthroline using various equivalents of 1,10-phenanthroline and 1,4-butane sultone under different conditions were not successful. This fail is probably because of the increased steric hindrance in the double linkers structure (PhBs₂, Scheme 1, 1b) and also probably because of the disterbing effect of the inhainced positive charge on the ring aromaticity that force 1,10-phenanthroline to be resistant against the intrance of the second linkage. In contrast, both of the mono linker structure and double linkers structure of 1.4-dimethylpipirazine were successfuly obtaind by using different experimental conditions. To achieve the mono linker structure (PipBs₁, Scheme 2, 2a), 1,4dimethylpiperazine and 1,4-butane sultone were reacted in 1:1.5 molar ratio at room temperature for 12 h while for the preparation of PipBs₂ (Scheme 2, 2b), 1:3 molar ratio of 1,4-dimethylpiperazine and 1,4butane sultone were reacted at 60° C for 24 h.



3.2 Characterization of the catalysts

3.2.1 IR spectra

The FT-IR technique is quite useful to identify or conform the structural and bonding changes in the Keggin unit present in the prepared BAILs-PW comparing to that of the neat $H_3PW_{12}O_{40}$. FT-IR spectra of [PhBs₁]₃-PW catalyst, neat $H_3PW_{12}O_{40}$ and pristine 1,10-phenanthroline are illustrated in Fig. 1. In the FT-IR spectrum of 1,10-phenanthroline strong bands are observed in two frequency regions, namely from

700 to 900 cm $^{-1}$ and from 1400 to 1650 cm $^{-1}$. The strong bands at 738 cm $^{-1}$ and 854 cm $^{-1}$ have been assigned to the out of the plane motion of the hydrogen atoms on the heterocyclic rings, and to the hydrogen on the center ring respectively. Most intense and characteristic bands in the vibrational spectrum of 1,10-phenanthroline appear in the region 1400 to 1600 cm⁻¹. All of these bands involve C — C and C — N stretching vibrations. Four other bands can be assigned to C — C and C — N vibrations, two of which give rise to symmetric and two anti-symmetric in plane ring deformation frequencies (Fig. 1a). FT-IR spectrum of PWA shows specific absorption bands correspond to the Keggin structure at 802, 891, 979 and 1079 cm⁻¹ which are assigned to the stretching vibrations v_{as}(W–Oe–W), v_{as}(W–Oc–W), v_{as}(W–Ot) and v_{as}(P–O*), respectively (Fig. 1b). From the FT-IR spectrum of [PhBs₁]₃-PW (Fig. 1c), in spite of the slight shift of four featured peaks positions, are appeared distinctively (800, 894, 977, 1078 cm^{-1}) which indicates that the Keggin structure of $H_3PW_{12}O_{40}$ was well reserved after the protons in the H₃PW₁₂O₄₀ were substituted by the organic cation. On the other hand, S=O stretching vibrations at 1153 and 1230 cm⁻¹ were observed to confirm the presence of sulfonic group in [PhBs₁]₃-PW catalyst. Finally, the characteristic peaks of pristine 1,10-phenanthroline are obviously presented in the FT-IR spectrum of [PhBs₁]₃-PW.These observations are clear proofs for the combination of organic cation (PhBs₁) with H₃PW₁₂O₄₀ via ionic interactions to produce a new catalyst of organic PWA salt.



Fig. 1 FT-IR spectrum of pristine 1,10-Phenanthroline (a), $H_3PW_{12}O_{40}$ (b) and [PhBs₁]₃-PW catalyst (c)



 $\label{eq:Fig.2} \textbf{Fig. 2} \ FT-IR \ spectrum \ of \ pure \ 1,4-dimethylpiperazine \ (a), \ [PipBs_1]_3-PW \ (b) \ [PipBs_2]_3-(PW)_2 \ (c) \ H_3PW_{12}O_{40} \ (d)$

The FT-IR spectra of pure 1,4-dimethylpiperazine, $[PipBs_1]_3$ -PW and $[PipBs_2]_3$ -(PW)₂ are shown in Fig. 2. Again, herein distinctive featured peaks of $H_3PW_{12}O_{40}$ are clearly observable in the FT-IR spectra of $[PipBs_1]_3$ -PW and $[PipBs_2]_3$ -(PW)₂ that confirm the successful preparation of these new BAILs-PW catalysts.

3.2.2 NMR spectra of PhBs₁, PipBs₁ and PipBs₂

In the ¹HNMR spectrum of PhBs₁ four featured peaks positions are appeared in the aliphatic region which are assigned to the eight hydrogens of butane sulfonate linker attached to one of the two 1,10-phenanthrolinum nitrogens which strongly confirms the successful preparation of organic PhBs₁ (Please see S1). The two triplet peaks (J = 7.6 Hz) give rise to CH₂-N⁺ (more deshielded δ 5.96 ppm) and CH₂-S (δ 2.46 ppm), two quintet peaks (J = 7.6 Hz) refer to the two middle methylene groups (N⁺-CH₂-CH₂-CH₂-CH₂-CH₂-S) of butane sulfonate linker (See S1b). The existence of butane sulfonate linker was additionally confirmed in ¹³C-NMR spectrum when four carbon peaks were observed in the aliphatic region of PhBs₁. Eight aromatic hydrogens of 1,10-phenanthrolinum were found in the aromatic region which have been slightly more deshielded than aromatic hydrogen of pure 1,10-phenanthroline (See S1c). Comparison of the hydrogen integrations in the aromatic and aliphatic regions approves the mono grafted butane sulfonate (PhBs₁) and confirms the unsuccessful preparation of PhBs₂.



Fig. 3 ¹HNMR (400 MHz, D₂O) spectrum of PipBs₁ (blue) and PipBs₂ (green)

The identification of PipBs₁ from PipBs₂ structure was simply confirmed with the comparsion of the chemical shifts of N-CH₃ groups from their ¹HNMR spectra. In ¹HNMR spectrum of PipBs₁, more deshielded N⁺-CH₃ group is appeared as a singlet peak at 3.02 ppm while N-CH₃ group is appeared as a singlet peak at 2.28 ppm. The ¹HNMR spectrum of PipBs₂ shows two singlet peaks for both deshielded N⁺-CH₃ groups at 3.22 and 3.24 ppm which indicated that the chemical environment around these groups are not completly chemical equivalent groups (Fig. 3). In another word, the structure of PipBs₂ is not completly symetrical or two methyl groups ocuppy almost different steric poistions. On the base of ¹HNMR principles, one of them has axial conformation which is more shielded (3.22 ppm) and another has equiterial conformation (3.24 ppm) [25]. From the ¹³C-NMR spectrum of PipBs₁ (see S2), the chemical shift of deshielded N⁺-CH₃ group was observed at 54 ppm while N-CH₃ was seen at 46.7 ppm.

3.2.1 EDX analysis

The EDX spectra of the fresh and reused catalysts show that the [PhBs₁]₃-PW, [PipBs₁]₃-PW and [PipBs₂]₃-(PW)₂ have organometalic composition. The EDX spectra of the fresh catalysts confirm the existence of butane sulfonate and phosphotangestate in the structure of the catalysts which is another proof for the successful preparation of target BAILs-PW catalysts. The EDX spectra of the fresh and reused [PhBs₁]₃-PW catalyst after 6 runs for the esterification reaction between acetic acid and n-butanol were prepared (See S3). The comparison of the elements and their weight percent in the fresh and reused catalyst are almost the same which indicating that the structure, composition and catalytic activity of [PhBs₁]₃-PW catalyst is remained with negligible changes after 8 runs (in agreement with negligible product yield differences during 6 runs in Fig. 4).

3.2.2 TG analysis

The TG analysis of three BAILs-PW catalysts indicated that all these catalysts are thermally stable up to 300 °C nearby. For example, $[PipBs_2]_3$ -(PW)₂ catalyst shows an endothermic peak of the DSC curve emerged at 160 °C which refers to the loss of water (mass loss 1%). After this step, three step by step exothermic peaks above 300 °C (320, 475 and 600 °C) are arisen. Most probably, $[PipBs_2]^+$ cation is decomposed in the first and second steps at 325 °C and 475 °C, then in continue, $[PW_{12}O_{40}]$ anion is decompounded at 600 °C nearby (See S4).

3.3 Optimization of the esterification reaction condition catalyzed by [PhBs₁]₃-PW, [PipBs₁]₃-PW and [PipBs₂]₃-(PW)₂

After synthesis and characterization of polyoxometalate-based ionic liquid salts, their catalytic role and activity were explored for the esterification reaction. In order to optimize the reaction conditions, the esterification reaction of acetic acid with n-butanol over various amounts of reactants and catalysts, at different temperatures was selected as model reaction (Table 1). Under neat condition at 110°C, no considerable ester product was observed even after 4 h (entry 1). By using PipBs₂ as catalyst, the reaction did not progressed again but when 0.2 g of pure H₃PW₁₂O₄₀ was added at 110 °C, a heterogeneous solidliquid biphasic system was observed and the reaction was progressed which after 2 h, 78% yield of the desired ester was obtained on the base of GC analysis (entries 2 and 3). When 0.1 g of [PhBs₁]₃-PW or [PipBs₁]₃-PW was used as catalyst, the target ester was obtained (entries 4 and 5). From entries 1-5, it is clear that the existence of acidic hydrogen is critical for the esterification reaction. By using each of [PhBs₁]₃-PW, [PipBs₁]₃-PW or [PipBs₂]₃-(PW)₂ as catalyst below 100°C, a heterogeneous solid–liquid biphasic system was observed due to the insolubility of the catalysts in monocarboxylic acid and monohydric alcohol reactants. The catalysts became liquid when the reaction mixtures were heated to 110°C with stirring however made heterogeneous liquid-liquid systems with the reactants but dissolvable with produced water. By increasing the molar ratio of alcohol to acid up to 1.2 and increasing amount of the [PhBs₁]₃-PW, [PipBs₁]₃-PW catalysts from 0.1 g to 0.25 g, the reaction times were decreased and stopped at 1.5 h while the yields of the reactions were improved (entries 7-13). The maximum yield (97%) of the ester was obtained when 0.15 g of [PipBs₂]₃-(PW)₂ was used as catalyst (entry 14). Larger amounts of the catalysts did not lead to shorter reaction time or higher yield of the produced ester (entries 15-19). By further enhancing the molar ratio beyond 1.2, acetic acid became diluted in the presence of excess amount of n-butanol and led to slight decrease in the obtained yield of target ester (entries 20-22). Consequently, 1.2 molar ratio of n-butanol to acetic acid was selected as the optimized molar ratio. Finally, by comparison of the obtained yields and the loading account of using [PhBs₁]₃-PW, [PipBs₁]₃-PW and [PipBs₂]₃-(PW)₂ catalysts, [PipBs₂]₃-(PW)₂ was selected as catalyst of choice to extend its generality in esterification reaction of various carboxylic acid and alcohols (entry 14).

3.4 Extend the generality of the catalytic activity

Under optimized reaction conditions, the esterification reaction of monocarboxylic acids with monohydric alcohols in the presence of the superior $[PipBs_2]_3$ - $(PW)_2$ catalyst was performed as shown in scheme 3 and table 2. From table 2, it can be clearly seen that good to excellent yields with complete selectivity for corresponding esters (100%) were achieved in all cases. The prolonged carbon chains in reactants did not significantly affect the high yields for esters (6c, 6g and 6j). However, reactants with benzyl group more or less lowered the yields (6d, 6e and 6k).

For all [PhBs₁]₃-PW, [PipBs₁]₃-PW and [PipBs₂]₃-(PW)₂ as catalyst in esterification reaction, after the mixtures were cooled to room temperature, the catalysts dissolved in the produced water precipitated at

the bottom layer as gelatinous solid, and the produced ester with unconverted reactants were at the upper liquid layer.

Entry	Molar ratio of <mark>ŔOH/RCOOH</mark>	T[°C]	Catalyst (g)	Time(h)	Yield(%) ^[a, b]
1	1	110	neat	4	Trace
2	1	110	PipBs ₂ (0.2 g)	4	Trace
3	1	110	$H_3PW_{12}O_{40}(0.2 \text{ g})$	2	78
4	1	80	[PhBs ₁] ₃ -PW (0.1 g)	3	60
5	1	100	[PipBs ₁] ₃ -PW(0.1 g)	3	70
6	1	110	[PipBs ₁] ₃ -PW (0.2 g)	3	90
7	1.2	110	[PhBs ₁] ₃ -PW (0.1 g)	3	85
8	1.2	110	[PipBs ₂] ₃ -(PW) ₂ (0.1 g)	3	90
9	1.2	110	[PhBs ₁] ₃ -PW (0.2 g)	2	85
10	1.2	110	[PipBs ₁] ₃ -PW (0.2 g)	2	87
11	1.2	110	[PipBs ₂] ₃ -(PW) ₂ (0.15 g)	2	91
12	1.2	110	[PhBs ₁] ₃ -PW (0.25 g)	1.5	90
13	1.2	110	[PipBs ₁] ₃ -PW (0.25 g)	1.5	93
14	1.2	110	[PipBs ₂] ₃ -(PW) ₂ (0.15 g)	1.5	97
15	1.2	110	[PipBs ₂] ₃ -(PW) ₂ (0.2 g)	1.5	96
16	1.2	110	[PipBs ₂] ₃ -(PW) ₂ (0.3 g)	1.5	97
17	1.2	110	$[PipBs_2]_3$ -(PW) ₂ (0.5 g)	1.5	96
18	1.2	110	[PipBs ₁] ₃ -PW (0.3 g)	1.5	92
19	1.2	110	[PhBs ₁] ₃ -PW (0.4 g)	1.5	91
20	1.3	110	[PipBs ₂] ₃ -(PW) ₂ (0.15 g)	1.5	92
21	1.4	110	[PipBs ₂] ₃ -(PW) ₂ (0.15 g)	1.5	89
22	1.6	110	[PipBs ₂] ₃ -(PW) ₂ (0.15 g)	1.5	86

Table 1. Optimization of esterification reaction of acetic acid and n-butanol in the presence of prepared catalysts

^a Obtained from GC analysis, ^b Using water segregator

		[PipBs ₂] ⁺ ₃ -(PW ₁₂ O ₄₀ ³⁻) ₂	
RCOOH	+ R'OH	► T 2=5(12 +0 /2 →	RCOOR'
4	5	110 °C, Reflux	6a-3l

Scheme 3. Esterification reaction catalyzed by [PipBs₂]₃-(PW)₂

Entry	RCOOH (4)	ŔOH (5)	[PipBs ₂] ₃ -(PW) ₂	Time(h)	Yield(%) ^[a]	Selectivity(%)
<mark>6a</mark>	Acetic acid	n-Butanol	0.15 g	1.5	94	100
<mark>6b</mark>	Acetic acid	Ethanol	0.15 g	1.5	96	100
<mark>6c</mark>	Acetic acid	Dodecanol	0.15 g	2	93	100
<mark>6d</mark>	Acetic acid	Benzyl alcohol	0.15 g	2.5	87	100
<mark>6e</mark>	Benzoic acid	n-Butanol	0.15 g	1.5	89	100
<mark>6f</mark>	Lactic acid	Ethanol	0.15 g	2	87	100
<mark>6g</mark>	Mandelic acid	Dodecanol	0.15 g	2	90	100
<mark>6h</mark>	Lauric acid	n-Butanol	0.15 g	1.5	92	100
<mark>6i</mark>	Lactic acid	Benzyl alcohol	0.15 g	2	87	100
<mark>6j</mark>	Mandelic acid	n-Butanol	0.15 g	2	92	100
<mark>6k</mark>	Benzoic acid	Ethanol	0.15 g	1.5	88	100
<mark>61</mark>	Lactic acid	Ethanol	0.15 g	1.5	96	100

Table 2. Esterification reaction of different carboxylic acids and alcohols in the presence of [PipBs₂]₃-(PW)₂ as catalyst

^a Obtained from GC analysis

3.4 Recoverability and Reusability of the catalysts

As mentioned above, after completion of the esterification reaction and cooling the mixtures down slowly, the catalyst is appeared at the bottom layer as gelatinous solid in the produced water. Thus, in all cases, the solid catalyst could be conveniently recovered simply by decantation (or filtration) and easily recycled into the next run. To study the recycling and reusability performance of the introduced BAILs-PW, the esterification of acetic acid with n-butanol was selected as model reaction. The esterification reaction was checked for six repeated runs (fresh + five consecutive runs) using each of [PhBs₁]₃-PW, [PipBs₁]₃-PW and [PipBs₂]₃-(PW)₂ as catalyst. The yield of the desired ester using these catalysts for six repeated runs is represented (Fig. 4). It is obvious that the yield difference between the first and 6th runs is not considerable for all of the introduced catalysts by taking into account the weight loss in the operation for recovering the catalysts. These observations indicate the still very slow deactivation for the catalysts. Additionally, the EDX analysis of [PhBs₁]₃-PW after six runs (see S3b) demonstrates a quite stable structure and very low leaching accounts of the catalyst elements after the repeated use of the catalyst indicating that the catalyst efficiency is almost completely maintained during 6 consecutive runs in agreement with the recoverability/reusability study data.



Fig. 4 Recycling of $[PhBs]^+_3PW$, $[PipBs_1]_3-PW$ and $[PipBs_2]_3-(PW)_2$ for the esterification reaction of acetic acid with n-butanol (6a). Conditions: Molar ratio of n-butanol/CH₃COOH = 1.2, loading of $[PhBs]^+_3PW$, $[PipBs_1]_3-PW=0.25$ g and $[PipBs_2]_3-(PW)_2=0.15$ g, T=110 °C, t=1.5 h

4 Conclusion

In conclusion, a new series of BAILs with the phosphotungstate anion was prepared and well characterized. The catalytic activity and reusability of the novel introduced acidic catalysts was examined for the esterification reaction of monocarboxylic acids with monohydric alcohols under optimized condition. It was found that [PipBs₂]₃-(PW)₂ is the superior catalyst for the esterification reaction. The catalysts showed excellent activity and was simply separable and reusable up to 6 runs. The EDX analysis and the recoverability/reusability study of the introduced catalysts over repeated runs proved quite stable structures with almost completely retained efficiency of catalysts. Other applications of these BAILs are under investigation in our lab.

List of abbriviations

S: Supplementary file

POM: polyoxometalate

BAIL: Brønsted Acidic Ionic Liquid

PhBs₁: 4-(1,10-phenanthrolin-1-ium-1-yl)butane-1-sulfonate

PipBs₁: 4-(1,4-dimethylpiperazin-1-ium-1-yl)butane-1-sulfonate

PipBs₂: 1,4-dimethylpiperazine-1,4-diium-1,4-diyl)bis(butane-1-sulfonate)

BAILs-PW: Brønsted acidic ionic liquids with phosphotungstate anion

 $[PhBs_1]_3\text{-}PW\text{: }[4\text{-}(1,10\text{-}phenanthrolium\text{-}1\text{-}yl)butane\text{-}1\text{-}sulfonate]_3PW_{12}O_{40}^{3\text{-}}$

[PipBs₁]₃-PW: [4-(1,4-dimethylpiperazin-1-ium-1-yl)butane-1-sulfonate]₃PW₁₂O₄₀³⁻

 $[PipBs_2]_3$ - $(PW)_2$: $[1,4-dimethylpiperazine-1,4-diium-1,4-diyl)bis(butane-1-sulfonate)]_3 (PW_{12}O_{40}^{-3-})_2$

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Novel SO₃H-functionalized polyoxometalate-based ionic liquids as highly efficient catalysts for esterification reaction

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Highlights

- > Three classes of novel SO₃H-functionalized polyoxometalate-based ionic liquids were synthesized
- > The esterification reactions were efficiently catalyzed in the presence of introduced ionic liquids
- > The catalysts were easily separable and reusable up to six runs
- > The procedure is simple and green
- > Very low leaching of the polyoxometalate anion was observed

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