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Sulfonated organic heteropolyacid salts: Recyclable green solid catalysts for esterifications

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ABSTRACT

A family of solid organic heteropolyacid (HPA) salts were prepared by combining Keggin heteropolyanions with ionic liquid (IL)-forming cations functionalized by propane sulfonate (PS). Their catalytic activities were evaluated in esterifications, including the testing of the influence of organic cations, function of heteropolyanions, scope of reactions, optimization of reaction conditions, and catalytic reusability. The obtained catalysts caused a liquid–liquid biphasic esterification system, presenting high yield and selectivity for target esters, and after reaction, they appeared in solid state again, which could be easily recovered and quite steadily reused demonstrated by a seven-run recycling test. The highly efficient and environmentally benign performance of this family of catalysts is due to the pseudoliquid behavior of HPA salts that allows PS acidic species in the bulk of the heteropoly compound acting fully as active centers for esterification, as well as the stabilization function of heteropolyanion on carbonium ion intermediates created at acid sites.

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1. Introduction

Heteropolyacids (HPAs) can be used as catalysts for numerous organic reactions because of their unique acidic and redox properties, nevertheless, the low surface areas ($<10 \text{ m}^2/\text{g}$) as solid catalysts and high solubility in polar reaction media largely hinder their practical utilizations [1]. To overcome these disadvantages, HPAs have been impregnated onto or encapsulated into porous carriers with high surface areas, such as silica, active carbon, zeolite, and so on [2–5]; however, these systems suffer from the high mass transfer resistance, the leaching of HPA active phase, or the tendency to deactivation. Another solution is to prepare water-tolerant HPA salts with considerable high surface areas ($>100 \text{ m}^2/\text{g}$) by partially exchanging protons of the parent HPA with large inorganic cations like Cs^+ , K^+ , Rb^+ and NH_4 [6], which still suffers from operation difficulties due to their small particle sizes [7]. Therefore, new modifications for HPA catalysts rather than the above mentioned routine approaches are greatly desired to broaden its catalytic applications.

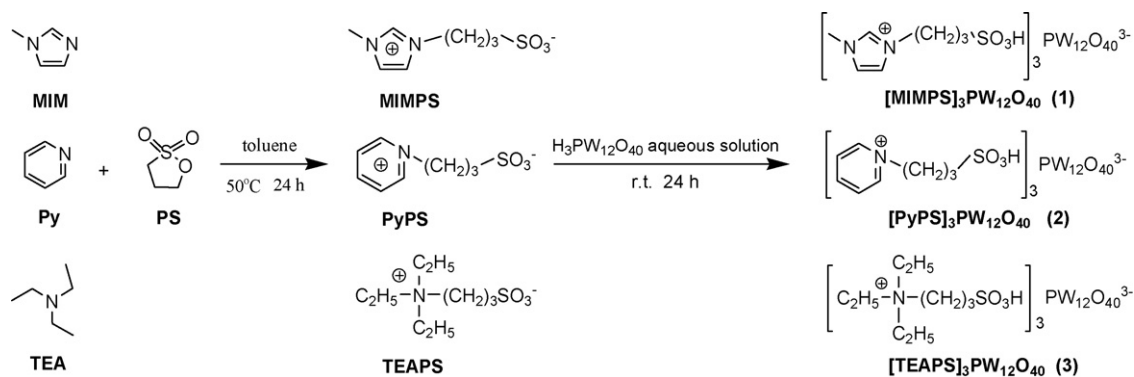
Organic–inorganic hybrid materials have been a great deal of research interest in the field of nanoelectronics, sensing, adsorption and catalysis due to the flexible tailorability of both organic

and inorganic groups. Among them, organic-functionalized silica and ionic liquids (ILs) are good examples [8–13]. It is known that ILs are formed by combining organic cations with inorganic anions through ionic linkage, with the inorganic anions always being univalent. On the other hand, the combination of organic species with HPAs can cause the formation of HPAs-based hybrid materials that are emerging to be very important in catalysis [14].

These previous findings stimulate us to make the combination of propane sulfonate (PS) functionalized organic cations with Keggin heteropolyanions with high valence, and the preliminary results have been recently reported as a communication [15]. We find that thus produced organic–inorganic hybrid materials are a family of new HPA salts with three IL-forming cations bonded ionically to an inorganic heteropolyanion. Nevertheless, they are not conventional ILs because their melting points are above 100°C . When the solid hybrids were used as catalysts for the esterification with one of reactants being a polycarboxylic acid or polyol, they acted as “reaction induced self-separation catalysts” due to their good solubility in reactants and nonmiscibility with ester product. However, one may want to know what would happen when they are used as catalysts in esterifications of monocarboxylic acids with monohydric alcohols. In this study, we report in detail the catalytic behavior of the PS functionalized organic–heteropolyanion hybrid materials in many of such common esterifications, mostly taking the esterification of acetic acid with *n*-butanol as a model reaction. The hybrids are revealed to be highly efficient green catalysts that can be easily recovered and quite steadily reused, with the catalyst's structure substantially unchanged.

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Scheme 1. Syntheses of catalysts.

2. Experimental

2.1. Materials and methods

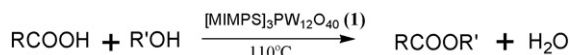
All chemicals were of analytical grade and used as received. FT-IR spectra for samples in KBr discs were recorded on a Nicolet 360 FT-IR instrument in 4000–400 cm^{-1} region. The concentration of reactants and product was directly measured by the gas chromatography (GC SP-6890, Lunan Ruihong of China).

2.2. Syntheses of organic HPA salt catalysts

1–3: The organic HPA salts were synthesized following the procedure in Scheme 1 according to our previous work [15]. For **1**, methylimidazole (9.02 g, 0.11 mol) and 1,3-propanesultone (12.21 g, 0.10 mol) were dissolved in toluene (100 mL) and stirred at 50 °C for 24 h under nitrogen atmosphere. A white precipitate (MIMPS) formed; it was filtered and washed with ether for three times, then dried in a vacuum. The resulting MIMPS (1.23 g, 0.006 mol) was added to the aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (5.76 g, 0.002 mol), followed by the stirring of the mixture at room temperature for 24 h. Water was removed in vacuum to give the final product as solid. $[\text{PyPS}]_3\text{PW}_{12}\text{O}_{40}$ (**2**), $[\text{TEAPS}]_3\text{PW}_{12}\text{O}_{40}$ (**3**), $[\text{MIMPS}]_4\text{SiW}_{12}\text{O}_{40}$, $[\text{MIMPS}]_3\text{PMo}_{12}\text{O}_{40}$, $[\text{TEA}]_3\text{PW}_{12}\text{O}_{40}$, $[\text{MIM}]_3\text{PW}_{12}\text{O}_{40}$, and $[\text{Py}]_3\text{PW}_{12}\text{O}_{40}$ were prepared based on the same method.

2.3. Procedure for esterification reactions

Taking the esterification of acetic acid with *n*-butanol as an example, the typical procedure for esterification reactions is as follows (see Scheme 2): acetic acid (1.80 g, 30 mmol), *n*-butanol (2.67 g, 36 mmol), and catalyst **1** (0.20 g, 0.06 mmol) were added to a round-bottomed flask with a water segregator (for a control test, the water segregator was not used). The resulting solution was refluxed at 110 °C for 1.5 h with vigorous stirring. The reaction mixture was cooled to room temperature. The top liquid layer was analyzed using the gas chromatography. Reaction conditions were changed to optimize the yield of ester. For other esterification reactions, the test was carried out accordingly. Exceptionally, for esterifications of acetic acid with benzyl alcohol, acetic acid with dodecanol and acetic acid with *n*-octanol, toluene was added as the water-carrying agent, and for esterification of acetic acid with ethanol, cyclohexane was added as the water-carrying agent.

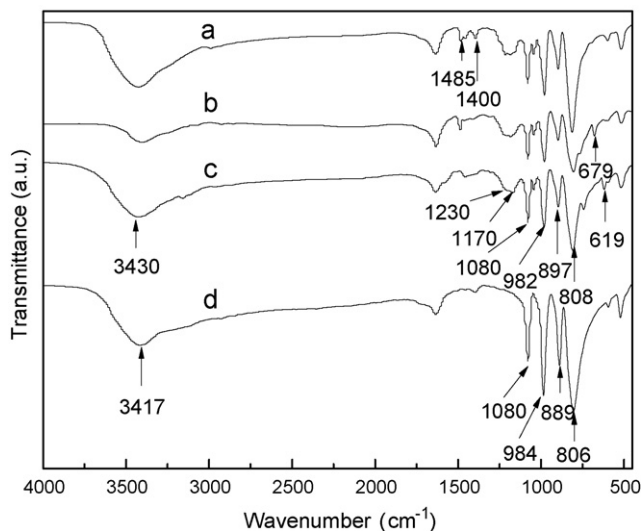


Scheme 2. Esterification of monocarboxylic acid with monohydric alcohol.

3. Results and discussion

3.1. Characterization of PS functionalized organic-phosphotungstate hybrids by FT-IR

Spectra of ^1H NMR, ^{13}C NMR and ESI-MS for the PS functionalized organic-phosphotungstate hybrids, $[\text{MIMPS}]_3\text{PW}_{12}\text{O}_{40}$ (**1**), $[\text{PyPS}]_3\text{PW}_{12}\text{O}_{40}$ (**2**) and $[\text{TEAPS}]_3\text{PW}_{12}\text{O}_{40}$ (**3**), were shown in the supporting information of our previous report [15], which demonstrated that the hybrid materials are HPA salts formed by the ionic bonding of three conventional IL-forming cations with an inorganic heteropolyanion. In this work, their FT-IR spectra are illustrated in Fig. 1, comparing with that of the neat $\text{H}_3\text{PW}_{12}\text{O}_{40}$. It can be seen that in wavenumber region of 800–1100 cm^{-1} , $\text{H}_3\text{PW}_{12}\text{O}_{40}$ gave four featured peaks (1080 (P–O_a), 984 (W=O_d), 889 (W–O_b–W) (corner-sharing), and 806 cm^{-1} (W–O_c–W) (edge-sharing)) assigned to the Keggin structure. For all the hybrid samples, in spite of the decrease of peak intensities and slight shift of peak positions, the four peaks appeared distinctively, which indicates that the Keggin structure of heteropolyanion was well reserved after the protons in the HPA were substituted by the organic cations. On the other hand, S=O stretching vibrations at 1230 and 1170 cm^{-1} were detected to verify the presence of sulfonic groups in catalysts. Furthermore, the hybrids exhibited the featured bands for organic groups, respectively; for example, **1** showed a band at 619 cm^{-1} that is attributed to the bending vibra-

Fig. 1. FT-IR spectra for hybrid catalysts and pure phosphotungstic acid, (a) **3**, (b) **2**, (c) **1** and (d) $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

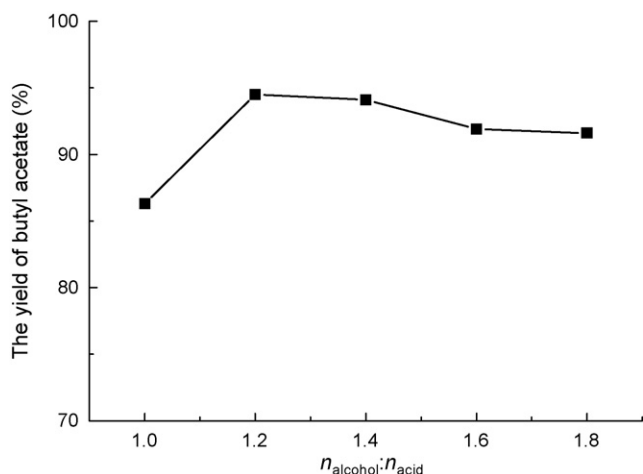


Fig. 2. Effect of molar ratio of alcohol to acid on the yield of butyl acetate in the esterification over **1**.

tion of the C–H bond in imidazole fragment, **2** gave a peak at 679 cm^{-1} due to the bending vibration of the C–H bond in pyridine, and **3** displayed two bands at 1485 and 1400 cm^{-1} because of the stretching vibration of the C–C bond and bending vibration of the C–H bond, respectively. These observations again confirm that the combination of PS functionalized organic cations with heteropolyanions via ionic linkage produces a new family of organic HPA salts, the composition of which is very similar to that of ILs.

The nature of ILs depends on the three-dimensional network of anions and cations by weak interaction between them, such as hydrogen bonds, van der Waals and Coulombic forces [16–18]. Looking into Fig. 1, we can see that the broad and asymmetric featured peak at 3417 cm^{-1} for pure $\text{H}_3\text{PW}_{12}\text{O}_{40}$ due to O–H vibrations clearly shifted to 3430 cm^{-1} when organic cations were combined with the heteropolyanion for **1–3** hybrids, which can be indicative of the existence of extended hydrogen bonding network between heteropolyanions and organic cations. It is suggested that the hydrogen bonding network also accounts for the slight shifts of the three featured peaks for the Keggin structure of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ to 982 cm^{-1} (W=O_d), 897 cm^{-1} (W–O_b–W) (corner-sharing), and 808 cm^{-1} (W–O_c–W) (edge-sharing) for hybrid materials, respectively. It is the network of hydrogen bonding, together with the large volume and high valence of the heteropolyanion that endow these hybrids with solid nature (m.p. above 100°C). Unlike conventional ILs, the solid acidic organic HPA salts can be readily used as solid catalysts.

3.2. Effect of reaction conditions

As a control experiment, esterification of acetic acid (30 mmol) with *n*-butanol (36 mmol) over **1** was carried out at 110°C for 1.5 h, without using a segregator to remove the produced water. Before starting the reaction at the room reaction temperature, a solid–liquid biphasic system was observed due to the insolubility of the catalyst in monocarboxylic acid and/or monohydric alcohol. However, the catalyst became liquid when the reaction mixture was heated to 110°C with stirring, and the liquid was insoluble in reactants but dissolvable with produced water. In this case, the reaction was a liquid–liquid biphasic system, giving 82.5% yield of butyl acetate with 100% selectivity. After the mixture being cooled to room temperature, the catalyst dissolved in the produced water precipitated at the bottom layer as a gelatinous solid, and the produced ester with unconverted reactants was at the upper liquid layer.

Esterification is known as a reversible reaction; therefore, in order to achieve a higher yield, it is necessary to remove the produced water as complete as possible to drive the reaction equilibrium forward. Actually, it was found to be true for the new hybrid catalyst **1** when we carried out the experiment to investigate the effect of molar ratio of alcohol to acid on the yield of ester with the produced water being removed in time by a water segregator, as shown in Fig. 2. When the molar ratio of alcohol to acid increased up to 1.2 without using any extra solvents, the maximum yield 94.5% was achieved, which is much higher than 82.5% obtained without removing the produced water. With further enhancing the ratio beyond 1.2, the yield decreased slightly due to the dilution of acetic acid by the excess *n*-butanol. 1.2 is selected as the suitable molar ratio of *n*-butanol to acetic acid, which is consistent with the practical situation in industry, where the excess amount of alcohol is often employed over acid.

Fig. 3 plots the effect of reaction temperature on the yield of the ester over catalyst **1**. It can be seen that the increase of reaction temperature from 90 to 130°C led to the enhancement of the yield of butyl acetate, and above 110°C , the escape of the non-reacted acetic acid and *n*-butanol by evaporation also became noticeable, which results in the decrease of the yield. The maximum yield 94.5% was observed at 110°C that should be the suitable reaction temperature.

Influence of reaction time on the yield of butyl acetate over catalyst **1** is displayed in Fig. 4. It can be seen that the remarkable increase in yield along with the prolongation of reaction time stopped at 1.5 h, beyond which the constant yield around 95% was observed. As compared with the reaction time (2–6 h) in previous reports concerning the conventional PS functionalized IL catalysts/solvents for esterification [19,20], the new catalyst **1** gives rise to a rather high yield of the ester within a shorter reaction time.

Fig. 5 represents the effect of catalyst amount on the yield of the ester in esterification of acetic acid with *n*-butanol over catalyst **1**. When the catalyst amount changed from 0 to 0.30 g, the yield of butyl acetate increased smoothly from 37.7% to 94.5% and thereafter remained almost constant. Nowadays, the conventional ILs functionalized by sulfonic acid have been investigated widely as acidic catalysts in esterification. Nevertheless, they are used as both solvent and catalyst, so a large amount (concentration) of ILs (usually 20–300 mol%) were required in reaction media [21–24]. For example, alkane sulfonic acid functional group was first introduced into ILs by Davis and his co-workers [24], and they used them as dual solvent/catalyst for esterification observing the phenomenon of temperature-controlled liquid–solid separation. In contrast, Fig. 5 gives an optimal catalyst amount of 0.2 g, corre-

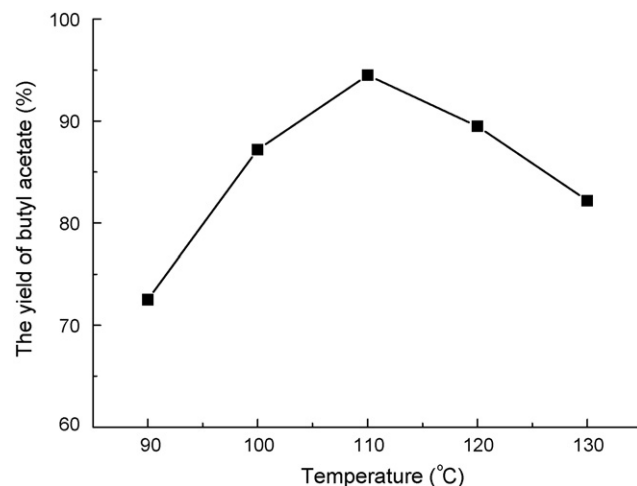


Fig. 3. Effect of reaction temperature on the yield of butyl acetate in the esterification over **1**.

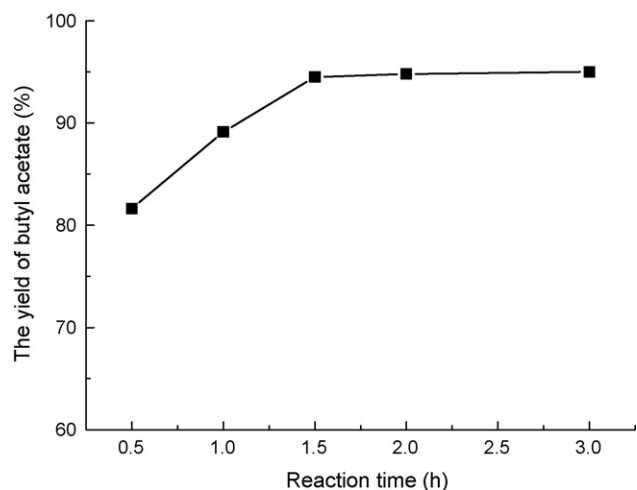


Fig. 4. Effect of reaction time on the yield of butyl acetate in the esterification over 1.

sponding to a very low molar ratio 1:500 of the catalyst to acetic acid (catalyst 0.06 mmol to the acetic acid 30 mmol), which indicates that the organic–HPA hybrid synthesized in this work acts indeed as a solid catalyst.

3.3. Effect of organic cations in catalysts on esterification of acetic acid with *n*-butanol

Table 1 lists the results of esterification of acetic acid with *n*-butanol over the synthesized HPA salts with different organic cations. As the strongest acid among HPAs due to the three protons in the cation position [25–27], pure $H_3PW_{12}O_{40}$ presented a yield of ester 88.2% (entry 2). Nevertheless, the reaction proceeded in a homogeneous system, which makes catalyst recovery very difficult.

When the protons were totally substituted by the non-PS functionalized cations, the obtained organic HPA salts caused liquid–solid biphasic media due to their very high insolubility, but only gave low yields of ester, somewhat very similar to the non-catalyst system (entries 1 and 3–5), which implies that the PS-free samples have lost their acidity. Contrarily, the PS functionalized catalysts (entries 6–8) exhibited very high yields of ester (more than 94%), which are even higher than that of pure $H_3PW_{12}O_{40}$. This verifies explicitly a very high activity of the acid site provided by PS in

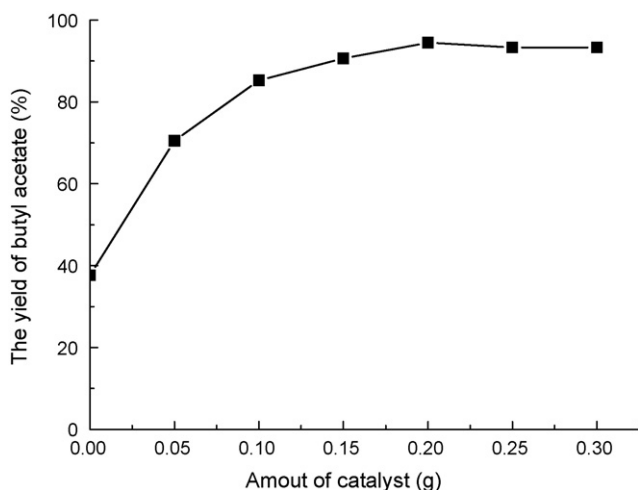


Fig. 5. Effect of catalyst amount on the yield of butyl acetate in the esterification over 1.

Table 1

Esterification of acetic acid with *n*-butanol over various catalysts with different organic cations^a.

Entry	Catalyst	Reaction phenomenon	Yield (%) ^b
1	Without catalyst	Homogeneous	37.7
2	$H_3PW_{12}O_{40}$	Homogeneous	88.2
3	$[MIM]_3PW_{12}O_{40}$	Heterogeneous (liquid–solid)	38.8
4	$[TEA]_3PW_{12}O_{40}$	Heterogeneous (liquid–solid)	41.9
5	$[Py]_3PW_{12}O_{40}$	Heterogeneous (liquid–solid)	39.0
6	$[MIMPS]_3PW_{12}O_{40}$	Heterogeneous (liquid–liquid)	94.5
7	$[TEAPS]_3PW_{12}O_{40}$	Heterogeneous (liquid–liquid)	95.2
8	$[PyPS]_3PW_{12}O_{40}$	Heterogeneous (liquid–liquid)	94.3

^a Reaction conditions: catalyst (0.06 mmol), acetic acid (30 mmol), $n_{alcohol}:n_{acid}$ (1.2:1), 110 °C, 1.5 h, with water segregator.

^b Yield of butyl acetate based on acetic acid.

organic cations of HPA salts. For the three PS functionalized solids, which are insoluble in reactant and product, the liquid–liquid biphasic heterogeneous reaction systems were observed at the reaction temperature 110 °C that is lower than the melting points of catalysts. The liquid phase of the catalysts is thus considered to relate with the small amount of water that could not be removed completely by the segregator.

3.4. Effect of heteropolyanions in catalysts on esterification of acetic acid with *n*-butanol

To explore the effect of inorganic anions, catalytic activities of PS functionalized imidazole (MIMPS) salts of $PW_{12}O_{40}^{3-}$, $PMo_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, and the conventional IL-forming anion HSO_4^- in the esterification of acetic acid with *n*-butanol are compared in Table 2. It can be seen that PS functionalized imidazole (MIMPS) salts of $PMo_{12}O_{40}^{3-}$ and $SiW_{12}O_{40}^{4-}$ anions (entries 5 and 6) showed the same phenomenon and very comparable activities to that of $PW_{12}O_{40}^{3-}$, and their activities were clearly higher than those of pure $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ (entries 2 and 3). The conventional acidic IL catalyst $[MIMPS]HSO_4$ exhibited a low yield of 65.6% (entry 7) even in a homogeneous system with the amount of $[MIMPS]HSO_4$ being 0.33 mmol, which was much higher than 0.06 mmol for the other catalysts in Table 2.

Although the PS acid sites in organic cations work as the active centers for esterification, Keggin heteropolyanions are still considered to play very significant roles in achieving such high activities. On the one hand, the heteropolyanions make the IL-like hybrid materials solid acids, and on the other hand, the presence of hierarchical structures of HPA catalysts can lead to surface-type and pseudoliquid (bulk-type (I) and bulk-type (II)) catalysis modes [28–31]. In this work, both reactants (acid and alcohol) were polar and thin molecules, so the pseudoliquid behaviour in the catalysis of esterification can be workable for the newly synthesised organic HPA salts. Therefore, although suppositively, we proposed a

Table 2

Esterification of acetic acid with *n*-butanol over various catalysts with different inorganic anions^a.

Entry	Catalyst	Reaction phenomenon	Yield (%) ^b
1	$H_3PW_{12}O_{40}$	Homogeneous	88.2
2	$H_4SiW_{12}O_{40}$	Homogeneous	79.4
3	$H_3PMo_{12}O_{40}$	Homogeneous	87.0
4	$[MIMPS]_3PW_{12}O_{40}$	Heterogeneous (liquid–liquid)	94.5
5	$[MIMPS]_3PMo_{12}O_{40}$	Heterogeneous (liquid–liquid)	96.1
6	$[MIMPS]_4SiW_{12}O_{40}$	Heterogeneous (liquid–liquid)	90.2
7 ^c	$[MIMPS]HSO_4$	Homogeneous	65.6

^a Reaction conditions: catalyst (0.06 mmol), acetic acid (30 mmol), $n_{alcohol}:n_{acid}$ (1.2:1), 110 °C, 1.5 h, with water segregator.

^b Yield of butyl acetate based on acetic acid.

^c Catalyst amount 0.33 mmol.

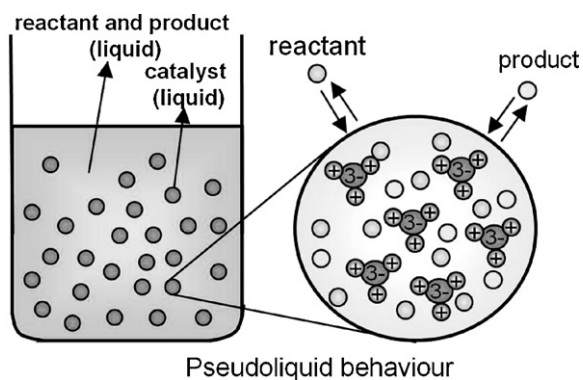


Fig. 6. Schematic diagram of the esterification of acetic acid with *n*-butanol over the organic HPA salt catalyst.

possible reaction diagram for the esterification with [MIMPS]PW₁₂O₄₀ as the catalyst in Fig. 6. Despite of the biphasic reaction system, reactant molecules could penetrate into the second structure of heteropolyanions to contact easily with acid active sites of PS in organic cations, where the reaction intermediate (carbonium ion) and final product (ester) are generated. Thus, the esterification mostly takes place inside the HPA salt phase, which allows the PS species giving full play as active centres, just as what would happen in a homogeneous system. Another important role of heteropolyanions is the stabilization function on carbonium ion intermediates created at acid sites in the bulk of the organic HPA salts [32–34], which is able to facilitate the creation of ester. This proposal may account for the higher yields on heteropolyacid salts (entries 4–6 of Table 2) than that on the conventional IL salt (entry 7 of Table 2); however, more direct evidences are need to verify it.

On the other hand, in view of economical and environmental concerns, it is very desirable to immobilize conventional ILs onto porous carriers and to use them as solid catalysts [33–37]. In this work, IL-forming cations are combined with heteropolyanions to make solid acids, which, in our opinion, may be a new strategy to create solid catalysts with IL-like composition.

3.5. Catalytic performance of **1** in various esterification reactions

Esterification is important process to manufacture a variety of intermediates and end-products, such as fragrances, monomers, solvents, plasticizers, etc [20]. For esterifications with one of reactants being a polycarboxylic acid or polyol, our previous report [15] have demonstrated high activities of the organic HPA salts accompanying with a green process of “reaction-induced self-separation catalysts”. In this work, various esterifications of monocarboxylic acids with monohydric alcohols are investigated on **1**, as shown in

Table 3. For reactions in entries 9 and 10, owing to the high polarity of lactic acid or mandelic acid that involves two strong polar sites in the molecule, reaction-induced phase-transfer reaction systems (switching from a homogeneous to liquid–solid biphasic heterogeneous system) were clearly observed, which is very similar to the phenomenon described in our early findings [15]. The other entries were liquid–liquid biphasic heterogeneous systems. It can be seen from Table 3 that good to excellent yields with perfect selectivity for corresponding esters (100%) were obtained in all cases (except entry 1). The prolonged carbon chains in reactants almost did not obstruct the high yields for esters (entries 2, 4, 6 and 7). Reactants with benzyl group more or less lowered the yields (entries 1 and 8), especially for the esterification of acetic acid with benzyl alcohol. It is noteworthy that the later is rather difficult reaction that could not give a high yield of carbobenzyloxy acetate as well over other catalysts, such as 12-silicotungstic acid supported on zirconia-embedded SBA-15, and 1-butylpyridinium chloride–aluminium(III) chloride [38,39].

3.6. Catalyst recoverability and reusability

For esterifications in entries 1–8, Table 3, the synthesized PS functionalized hybrid catalysts resulted in a similar liquid–liquid biphasic reaction system at their reaction temperatures. An interesting phenomenon was that upon the cooling of the reacted mixture to room temperature, the catalyst turned to be a transparent solid appeared at the bottom of the reactor, with the produced ester with unconverted reactants remained as liquid at the upper layer. For entries 9 and 10, at the end of reaction, the catalyst also appeared as a solid. Thus, in all cases, the solid catalyst could be conveniently recovered simply by decantation (or filtration) and easily recycled into the next run. A seven-run recycling performance of **1** was investigated in the esterification of acetic acid with *n*-butanol, and the results are shown in Fig. 7. It is obvious that the yield of ester 94.5% for the first run only marginally decreased down to 87% for the third run, and after that, it was rather stable during the repeated usage up to seven times. At the seventh reaction run, 82.3 wt% of the catalyst (compared to the amount of fresh one used in the first run) was recovered and 84.4% yield was obtained. One can see from Fig. 5 that, if using the same amount of fresh catalyst ($0.2 \times 82.3\% = 0.165$ g) for the seventh run of reaction, the yield should be approximately 91.3% that is still higher than that of the recovered catalyst (84.4%). This indicates the still very slow deactivation for the catalyst, mostly happening during the first three runs (see Fig. 7), even taking into account of the weight loss in the operation for recovering the catalyst. As illustrated in Fig. 8, the profile of IR spectra for the recovered catalyst after the seventh run was well consistent with that of the fresh one, demonstrating a quite stable structure after the repeated use of the catalyst. However,

Table 3
Results of different esterifications of monocarboxylic acids with monohydric alcohols over **1**^a.

Entry	Carboxylic acid (A)	Alcohol (B)	Temperature (°C)	Time (h)	$n_B:n_A$	Yield (%) ^b	Selectivity (%) ^c
1	Acetic acid	Benzyl alcohol	110	3	1:1.2	69.2	100
2	Acetic acid	Dodecanol	110	2	1:1.4	94.6	100
3	Acetic acid	Ethanol	90	1.5	1.2:1	83.6	100
4	Acetic acid	<i>n</i> -Octanol	110	2	1.2:1	93.2	100
5	Acetic acid	<i>n</i> -Butanol	110	1.5	1.2:1	94.5	100
6	Lauric acid	<i>n</i> -Butanol	120	2	1.2:1	91.4	100
7	Palmitic acid	<i>n</i> -Butanol	120	3	1.2:1	87.5	100
8	Benzoic acid	<i>n</i> -Butanol	130	4	3:1	82.1	100
9	Lactic acid	<i>n</i> -Butanol	110	2	3:1	85.5	100
10	Mandelic acid	<i>n</i> -Butanol	120	3	4:1	95.2	100

^a Reaction conditions: catalyst **1** (0.06 mmol), carboxylic acid (30 mmol), entries 1 and 2 alcohol (30 mmol), with water segregator; other conditions such as temperature, time and molar ratio of the two reactants were optimal ones for the individual reaction.

^b Yield for the ester based on carboxylic acid, entries 1 and 2 based on alcohol.

^c Selectivity for ester.

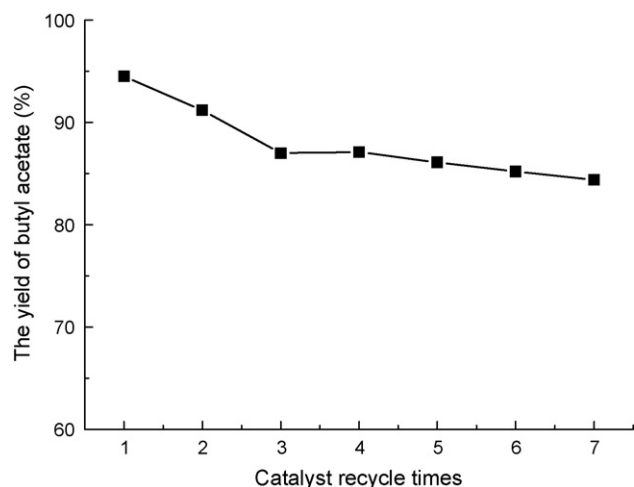


Fig. 7. Catalytic reusability of **1** for the esterification of acetic acid with *n*-butanol.



Fig. 8. The FT-IR spectra of (a) fresh **1** catalyst, (b) recovered **1** catalyst after the seventh run.

the intensities of IR bands decreased to some extent, which might be indicative of the slight deactivation of the recovered catalyst. Another observation from Fig. 8 is that not any bands assigned to the reactants and the ester in the recovered catalyst were detected, which strongly suggests that the dissolution of the liquids in the esterification medium into the solid organic HPA salt at the finish of reaction is negligible.

4. Conclusion

This work synthesizes a family of solid organic–inorganic hybrid materials by combining PS functionalized IL-forming organic cations with Keggin-structured heteropolyanions. In spite of the IL-like composition, they are organic heteropolyacid salts with melting points above 100 °C due to the high valence of heteropolyanions and the formation of hydrogen bonding network

between cations and anions. It is noteworthy that when the obtained hybrid materials were used as catalysts for esterifications, they acted as heterogeneous catalysts in liquid–liquid biphasic reaction media at the reaction temperature, and upon cooling down of the reacted mixture, catalysts resumed their solid state that can be easily recovered and reused without substantially changing the original structure, demonstrated by a seven-run test. This study provides a new strategy to get a family of novel green solid acid catalysts. We consider that the protocol can be very useful to design new HPA-type (maybe also IL-type) catalysts due to the high tailorability in both organic cations and heteropolyanions.

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