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Short Communication

Clean benzylation of anisole with benzyl alcohol over recyclable partially sulfonated imidazole-exchanged heteropoly phosphotungstate

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ABSTRACT

A series of organic heteropoly acidic salts with high acid strength have been prepared via the partial replacement of protons in a neat phosphotungstic acid. These hybrid catalysts have exhibited good activity and selectivity in the benzylation of anisole with benzyl alcohol. The "liquid-phase reaction at high temperature, solid-state separation at room temperature" performance of obtained hybrid catalysts enables an easy recovery and steady reusability demonstrated by a three-run recycling test.

1. Introduction

The benzylation of aromatic compounds to produce diarylmethanes and their derivatives, which are key industrial compounds as pharmaceutical intermediates or fine chemicals, is one of the important reactions in organic chemistry [1,2]. The general benzylation methods, using benzyl chloride as reagent or employing homogeneous acid catalysts such as $AlCl_3$, $FeCl_3$, and H_2SO_4, suffer from many problems like pollution, corrosion and difficulty in the separation and recovery of catalysts [3–5]. Considering that benzyl alcohol (BA) is a relatively friendly benzylation reagent due to water as the byproduct, a cleaner benzylation route can be carried out to reduce environmental pollution [6,7]. Solid catalysts have been studied in benzylation reactions with benzyl alcohol to overcome the problems of mineral acids [8,9]. However, these heterogeneous catalysts have disadvantages as well, for example, water instability, the tendency to deactivate, and high mass transfer resistance.

Acidic functionalized ionic liquids have been revealed as promising green acid catalysts in view of their high activity, easiness in separation and recovery, just like the advantages of both homogeneous and heterogenous catalysts [10,11]. Especially, owing to the variety of ionic liquid structure available, "temperature-controlled liquid–solid separation" or "reaction-controlled phase-transfer" catalysis can be actualized by ionic liquid catalysts [10,12]. The organic salts of heteropolyacids, which possess the structural characteristics of both ionic liquids and heteropoly compounds, have raised much concern as novel "task-specific" catalysts for acid catalyzed reaction [13]. Shi [14] employed $[BMIM]_3PW_{12}O_{40}$($[1\text{-butyl-3-methylimidazolium}]_3PW_{12}O_{40}$) as the catalyst for esterification of ethanol with acetic acid. Ivanova [15] studied the catalytic performances of $[BMIM]_3PW_{12}O_{40}$ and $[BMIM]_3PMo_{12}O_{40}$ in the dehydration of methanol. Dai [16] found that $[HMIM]_3PW_{12}O_{40}$($[1\text{-methylimidazolium}]_3PW_{12}O_{40}$) could form a "temperature-controlled phase-separation" system in the acetalation reaction of carbonyl compounds. Leng [13,17] synthesized a series of heteropoly ionic liquids containing propane sulfonate (PS) functionalized organic cations $[MIMPS]_3PW_{12}O_{40}$($[3\text{-(1-methylimidazolium-3-yl)propane-1-sulfonate}]_3PW_{12}O_{40}$), $[PyPS]_3PW_{12}O_{40}$ ($[\text{pyridinium propane sulfonate}]_3PW_{12}O_{40}$) and $[TEAPS]_3PW_{12}O_{40}$($[3\text{-(triethylammonio)propane sulfonate}]_3PW_{12}O_{40}$). It was found that the use of the PS group was an effective approach to improve the acid strength of heteropoly ionic liquids. More importantly, $PW_{12}O_{40}^{3-}$ existing in the catalysts would lead to higher melting points than conventional ionic liquids. The above heteropoly ionic liquids with solid nature could act as "reaction induced self-separation catalysts" in some esterification reactions due to their different solubility in reactants and products. However, the PS group in organic cations could only provide enough acid strength for some specific reactions which were easy to realize, such as esterification [18–20]. In our benzylation study of aromatic compounds with benzyl alcohol using $[MIMPS]_3PW_{12}O_{40}$, considerable dibenzyl ether (DBE), the dehydrated product of benzyl alcohol, was produced due to insufficient acid strength of the catalyst.

In this paper, heteropoly acidic salts with acid strength even higher than a neat phosphotungstic acid have been prepared via the partial replacement of protons by the organic cation with highly acidic PS groups. These heteropoly acidic salts, which have enough water resistance and the similar structure of ionic liquids, have exhibited good activity, selectivity and stability in the benzylation of anisole with benzyl alcohol.

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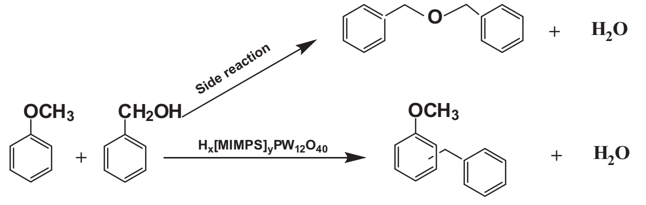

Scheme 1. Benzylation of anisole with benzyl alcohol.

What's more, designed catalysts can be readily reused according to their "liquid-phase reaction at high temperature, solid-state separation at room temperature" performance.

2. Experimental

2.1. Materials and methods

All chemicals were of analytical grade and used without further purification. The ^1H NMR spectra of the designed catalysts were recorded with a 500 MHz BRUKER spectrometer in D_2O or DMSO. FT-IR spectra for catalyst samples in KBr disks were recorded on a Nicolet iS10 FT-IR instrument. Melting points of the catalysts were measured by a conventional method using X-4 type micromelting point apparatus. TG analysis was carried out with NETZSCH-TG 209 F1 Libra instruments in dry N_2 at a heating rate of 20 °C/min from 30 to 800 °C.

The acidity of prepared catalysts was determined by potentiometric titration [14,21]. A mixture containing 0.5 g sample and 30 mL acetonitrile was mixed with the stable potential. Then it was titrated with 0.05 mol/L acetonitrile solution of $n\text{-}C_4H_9NH_2$. The initial and jump potential values were registered by a pH meter to determine the acid strength and total acid amount of catalyst samples.

2.2. The preparation of hybrid catalysts

$[HMIM]_3PW_{12}O_{40}$ was obtained from Keggin phosphotungstic acid and N-methyl imidazole at room temperature [16]. $[BMIM]_3PW_{12}O_{40}$ was prepared from 1-butyl-3-methylimidazolium bromide ([BMIM]Br) and heteropolyacids $H_3PW_{12}O_{40}$ [14,22].

The sulfonated imidazole cations partially-exchanged heteropoly acid phosphotungstate $H_x[MIMPS]_yPW_{12}O_{40}$ $(x + y = 3)$ was synthesized following the below procedure [17]. N-methylimidazole (0.10 mol) and 1,3-propanesultone (0.10 mol) were dissolved in 100 mL toluene and stirred at 50 °C for 24 h under nitrogen atmosphere. The white precipitate MIMPS was filtered, washed with acetic ether for three times and dried in a vacuum for 4 h. The aqueous solution of $H_3PW_{12}O_{40}$ was dropped into the stoichiometric intermediate MIMPS to obtain acidic salts. The mixture was stirred at room temperature for 24 h, then was distilled and dried in a vacuum to give heteropoly acid phosphotungstate $H_x[MIMPS]_yPW_{12}O_{40}$ $(x + y = 3)$.

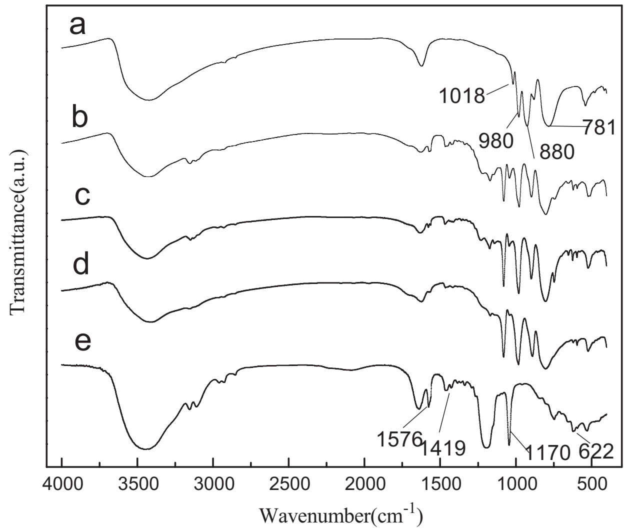

Fig. 1. FT-IR spectra for hybrid catalysts, (a) $H_3PW_{12}O_{40}$ (b) $[MIMPS]_3PW_{12}O_{40}$ (c) $H[MIMPS]_2PW_{12}O_{40}$ (d) $H_2[MIMPS]PW_{12}O_{40}$ and (e) MIMPS.

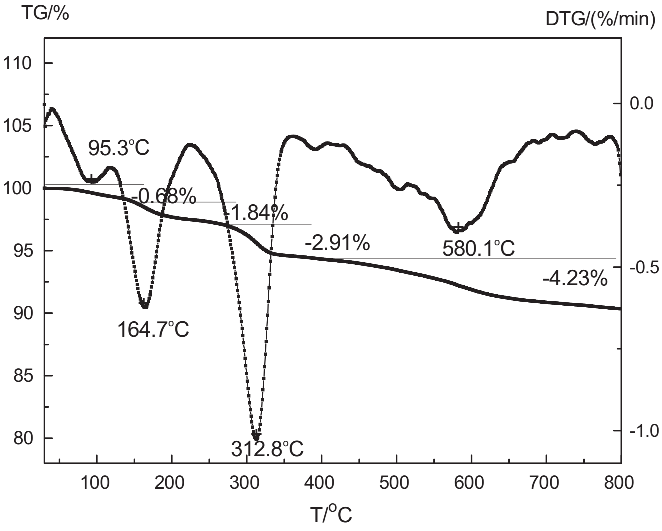

Fig. 2. TG–DTG profiles of $H_2[MIMPS]PW_{12}O_{40}$.

2.3. General procedure for the benzylation with benzyl alcohol

The typical procedure for benzylation reactions was as follows (see Scheme 1): Anisole, benzyl alcohol, and catalyst $H_x[MIMPS]_yPW_{12}O_{40}$ were added proportionally to a round-bottomed flask with a thermometer, a magnetic stirrer and a reflux condenser. The resulting reaction mixture was stirred vigorously at 160 °C for 2 h then was cooled to room temperature. The reaction solution, from which the generated water and precipitated catalyst had been removed, was analyzed using a gas chromatography(GC-9790) equipped with an FID detector and a capillary column (DB-35 ms, 30 m × 0.25 mm × 0.25 μm) to determine the conversion of benzyl alcohol and the selectivity of methoxy diphenyl methane (MDM) products.

3. Results and discussion

3.1. Characterization of hybrid catalysts

Similar ^1H NMR (500 MHz, DMSO) spectra of $[MIMPS]_3PW_{12}O_{40}$, $H[MIMPS]_2PW_{12}O_{40}$, $H_2[MIMPS]PW_{12}O_{40}$ and their intermediate are observed: δ 2.21(quint, 2H), 2.83(t, 2H), 3.83(s, 3H), 4.26(t, 2H), 7.38(d, 1H), 7.46(d, 1H), 8.70(s, 1H), which support the correct structure of organic cations. Moreover, their FT-IR spectra are illustrated in Fig. 1, comparing with that of the neat $H_3PW_{12}O_{40}$. It can be seen that $[MIMPS]_3PW_{12}O_{40}$, $H[MIMPS]_2PW_{12}O_{40}$ and $H_2[MIMPS]PW_{12}O_{40}$ catalysts gave similar four featured peaks (around 1018 (P–O), 980 (W=O), 880 ($W-O_{b1}-W$) and 781 cm^{-1} ($W-O_{b2}-W$)) with those of $H_3PW_{12}O_{40}$ assigned to the Keggin structure. On the other hand, featured peaks at 1576 (C=N), 1419 ($S-CH_2$), 1170 (S=O stretching vibration) and 622 (C–H of imidazole ring) cm^{-1} of MIMPS also appear in the spectra of all the hybrid catalysts. The above results indicate that both $MIMPS^+$ and $PW_{12}O_{40}^{3-}$ are combined in all the hybrid catalysts.

Fig. 2 shows that $H_2[MIMPS]PW_{12}O_{40}$ will lose crystalliferous water (calculated weight loss: 2.52%) during 30–275 °C. Moreover, decomposition peaks of the imidazole ring and sulfonic group in $MIMPS^+$ are

Table 1
Properties of hybrid catalysts.

Samples	Feature	Melting point (°C)	Solubility (25 °C)		Acid strength (mV)	Total acid amount (mmol/g)
			Water	Toluene		
$H_3PW_{12}O_{40}$	Faint yellow/white crystal	95	Yes	Not	702	0.791
$[BMIM]_3PW_{12}O_{40}$	White powder	>300	Not	Not	59	0.0159
$[HMIM]_3PW_{12}O_{40}$	White powder	>300	Not	Not	182	0.158
$[MIMPS]_3PW_{12}O_{40}$	Faint yellow crystal	110	Not	Not	602	0.264
$H[MIMPS]_2PW_{12}O_{40}$	White solid	145	Not	Not	698	0.562
$H_2[MIMPS]PW_{12}O_{40}$	Grayish white solid	79	Not	Not	715	0.782

Table 2
Catalytic benzylation performance of hybrid catalysts.[a]

Catalysts	Reaction phenomenon	Conv. of BA (%)	Product distribution (%)			
			2-MDM	4-MDM	DBE	Others[b]
$H_3PW_{12}O_{40}$	Catalyst was dissolved	99.3	46.1	53.9	–	–
$[BMIM]_3PW_{12}O_{40}$	Catalyst was insoluble	–	–	–	–	–
$[HMIM]_3PW_{12}O_{40}$	Catalyst was insoluble	–	–	–	–	–
$[MIMPS]_3PW_{12}O_{40}$	Catalyst was dissolved partly	97.8	19.5	24.0	55.7	0.8
$H[MIMPS]_2PW_{12}O_{40}$	Catalyst was dissolved at reaction temperature then separated out after cooling	99.2	49.4	50.5	–	0.1
$H_2[MIMPS]PW_{12}O_{40}$	Catalyst was dissolved at reaction temperature then separated out after cooling	99.5	43.3	55.3	–	1.4

[a] Reaction conditions: catalyst (0.10 mmol), anisole (0.05 mol), $n_{anisole}$:n_{BA} (1:1), reflux temperature, 2.0 h.

[b] Benzaldehyde and so on, and the same below.

observed at 312.8 °C and 580.1 °C respectively. The TG profile indicates that $H_2[MIMPS]PW_{12}O_{40}$ is quite stable up to 312.8 °C.

3.2. Acid property analysis of hybrid catalysts

According to the Brönsted Rules, the catalytic ability of the acid catalyst is proportional to its acid strength. A more effective way than introducing sulfonic acid group into cation to improve the acid strength of ionic liquids has not yet been found so far. In view of the superacidity of Keggin $H_3PW_{12}O_{40}$ and high charge of $PW_{12}O_{40}^{3-}$, organic-heteropoly acidic salts have been developed in this paper via the partial replacement of protons by the organic cations with highly acidic PS groups. It is as expected that the acid strength of prepared catalysts is close to that of neat phosphotungstic acid.

From the *n*-butylamine potentiometric titration results listed in Table 1, it can be seen that introducing organic cations into phosphotungstic acid to form normal salt will lead to a significant reduction in acid strength. Moreover, the acidic properties of normal salt hybrid catalysts rely on the structure of organic cations. Both acid strength and total acid amount of $[HMIM]_3PW_{12}O_{40}$ are higher than those of $[BMIM]_3PW_{12}O_{40}$ due to the proton on the N atom of the imidazole ring. Furthermore, sulfonic acid group can improve the acid strength of $[MIMPS]_3PW_{12}O_{40}$ greatly. However, it still cannot reach the acid strength level of neat $H_3PW_{12}O_{40}$. The total acid amount of $[MIMPS]_3PW_{12}O_{40}$ with sulfonic acid group(0.264 mmol/g) is higher than that of $[BMIM]_3PW_{12}O_{40}$ and $[HMIM]_3PW_{12}O_{40}$, but falls far below $H_3PW_{12}O_{40}$(0.791 mmol/g) because of the large volume and molar mass of organic cation. Nevertheless, $H_2[MIMPS]PW_{12}O_{40}$, the organic-heteropoly acidic salt of $H_3PW_{12}O_{40}$ prepared in this paper, possesses almost equivalent acid strength and total acid amount to neat phosphotungstic acid. On the other hand, unlike both phosphotungstic acid and conventional ILs, the prepared hybrids present solid nature and are insoluble in toluene and water at room temperature. As a result, $H_2[MIMPS]PW_{12}O_{40}$ can be used as a novel solid acid catalyst with superior super acidity and water resistance.

3.3. Catalytic performances of hybrids in the benzylation of anisole with benzyl alcohol

Catalytic performance of hybrids with different acid strengths in the benzylation of anisole with benzyl alcohol (BA) has been investigated under the same conditions. GC–MS results of reaction filtrate indicate that the DBE generated from the intermolecular dehydration process of BA is the main byproduct. Besides, a very small amount of benzaldehyde, the oxidation product of BA, is also found due to the catalytic oxidation ability of heteropoly compound. It can be seen from Table 2 that the hybrids without sulfonic acid group have no catalytic ability to transform BA into benzyl carbonium ion. On the other hand, because the O atom in BA molecule with higher cloud density can be attacked more easily than C atom in the benzene ring of anisole, the energy barrier of the reversible dehydration is lower than that of the benzylation. As a result, $[MIMPS]_3PW_{12}O_{40}$ with considerable acid strength will promote more BA turning into DBE instead of the target products MDM with a high conversion. When $H_3PW_{12}O_{40}$, $H[MIMPS]_2PW_{12}O_{40}$ or $H_2[MIMPS]PW_{12}O_{40}$ with high acid strength is used, the energy barrier of

Table 3
Effect of the molar ratio of reactants on the catalytic performance.[a]

$n_{anisole}$:n_{BA}	Conv. of BA (%)	Product distribution (%)			
		2-MDM	4-MDM	DBE	Others
1:1	99.5	43.3	55.3	–	1.4
1.3:1	99.2	46.2	51.0	2.1	0.7
1.5:1	99.8	45.8	50.6	2.4	1.2
2:1	99.9	47.8	51.3	0.3	0.6
3:1	99.8	45.9	48.6	0.3	5.2
4:1	99.4	51.0	42.0	7.0	–

[a] Reaction conditions: $H_2[MIMPS]PW_{12}O_{40}$ (0.10 mmol), benzyl alcohol (0.05 mol), reflux temperature, 2.0 h.

Table 4
Effect of the dosage on the catalytic performance.[a]

Dosage of catalyst (mmol)	Conv. of BA (%)	Product distribution (%)			
		2-MDM	4-MDM	BE	Others
0.05	99.7	34.8	41.1	23.1	1.0
0.075	99.4	48.2	51.8	–	–
0.10	99.5	43.3	55.3	–	1.4
0.15	98.9	49.2	50.8	–	–
0.20	99.3	48.5	51.5	–	–

[a] Reaction conditions: benzyl alcohol (0.05 mol), $n_{anisole}$:n_{BA} (1:1), reflux temperature, 2.0 h.

Table 5
Effect of reaction temperature on the catalytic performance.[a]

Reaction temperature	Conv. of BA (%)	Product distribution (%)			
		2-MDM	4-MDM	DBE	Others
80 °C	49.9	16.7	23.8	59.5	–
120 °C	99.8	29.7	35.6	33.7	1.0
155 °C	99.5	43.3	55.3	–	1.4

[a] Reaction conditions: $H_2[MIMPS]PW_{12}O_{40}$ (0.10 mmol), benzyl alcohol (0.05 mol), $n_{anisole}$:n_{BA} (1:1), 2.0 h.

benzylation is reduced. Accordingly, excellent results with both high conversion and good selectivity for MDM are obtained owing to the dominant position of irreversible benzylation. The difference of designed catalysts and $H_3PW_{12}O_{40}$ is that $H_3PW_{12}O_{40}$ is always dissolved in the reaction system and needs to be separated by distillation of reaction mixture, while $H[MIMPS]_2PW_{12}O_{40}$ and $H_2[MIMPS]PW_{12}O_{40}$ exhibit the characteristic of homogeneous catalysis at reaction temperature but depositing from system after cooling. This means that $H[MIMPS]_2PW_{12}O_{40}$ and $H_2[MIMPS]PW_{12}O_{40}$ possess high activity, good selectivity and ease of separation in the benzylation of anisole with BA at the same time. It can be seen from Tables 1 and 2 that the acidic salt hybrids, especially $H_2[MIMPS]PW_{12}O_{40}$ with higher acid strength and total acid amount, are excellent catalysts for benzylation.

To further investigate the catalytic performance of $H_2[MIMPS]PW_{12}O_{40}$, the effects of molar ratio of reactants, catalyst dosage, reaction temperature and reaction time have been tested and presented in Tables 3 to 6. It can be seen that all the above conditions have almost no effect on BA conversion (except reacted at 80 °C). More byproduct DBE will generate under the dosage of catalyst less than 0.05 mmol or the reaction temperature below 80 °C. This is because under the conditions of lower temperature and inadequate catalyst, it is more difficult to overcome the energy barrier of benzylation. Besides, slight effects of the above factors on MDM and 4-MDM selectivities have been caught sight of in the tables. Under optimized conditions: 0.10 mmol catalyst, 0.05 mol BA, $n_{anisole}:n_{BA} = 1:1$, reflux temperature (160 °C), 2.0 h, the selectivities of both MDM and 4-MDM can reach the highest values accompanied with almost all conversion of BA.

3.4. Reusability of hybrid catalyst

The reusability of the designed $H_2[MIMPS]PW_{12}O_{40}$ hybrid catalyst with “liquid-phase reaction at high temperature, solid-state separation at room temperature” performance constitutes one of its principal advantages. To test its reusability, the catalytic performance of fresh and reused $H_2[MIMPS]PW_{12}O_{40}$ in the benzylation of anisole by BA is listed in Table 7. It can be found that the fresh catalyst gives a desired result that almost all BA had been converted to the target products MDM under the above optimum conditions. Correspondingly, the third reused catalyst presents 87.6% conversion of BA and 97.8% selectivity for MDM respectively. These results indicate that $H_2[MIMPS]PW_{12}O_{40}$ hybrid catalyst can maintain good activity and selectivity even after three cycles. The decline of conversion can be ascribed to the loss of catalyst in the reaction system. FT-IR spectra for the hybrid catalysts before and after use (Fig. 3) confirm that no structural transformation has taken place for $H_2[MIMPS]PW_{12}O_{40}$ during reactions. Such catalytic performance is of great importance to potential industrial application.

Table 6
Effect of reaction time on the catalytic performance.[a]

Reaction time	Conv. of BA (%)	Product distribution (%)			
		2-MDM	4-MDM	DBE	Others
1 h	99.4	47.7	51.5	0.8	–
2 h	99.5	43.3	55.3	–	1.4
3 h	99.6	48.0	51.7	0.3	–
4 h	99.1	48.2	51.4	–	0.4
5 h	99.3	48.3	50.8	0.9	–

[a] Reaction conditions: $H_2[MIMPS]PW_{12}O_{40}$ (0.10 mmol), anisole (0.05 mol), $n_{anisole}$:n_{BA} (1:1), reflux temperature.

Table 7
Catalytic reusability of $H_2[MIMPS]PW_{12}O_{40}$ for the benzylation of anisole with benzyl alcohol.[a]

Catalyst recycle times	Conv. of BA (%)	Product distribution (%)			
		2-MDM	4-MDM	DBE	Others
0	99.7	46.6	53.4	–	–
1	92.9	45.1	51.5	0.6	2.8
2	93.0	44.2	51.3	0.7	3.8
3	87.6	45.5	52.3	1.2	1.0

[a] Reaction conditions: catalyst (0.10 mmol), benzyl alcohol (0.05 mol), $n_{anisole}$:n_{BA} (1:1), reflux temperature, 2.0 h.

4. Conclusions

$H_x[MIMPS]_yPW_{12}O_{40}$ $(x + y = 3)$, solid organic-heteropolyacid hybrid catalysts with high acid strength have been prepared via the partial replacement of the protons in a neat phosphotungstic acid by the sulfonated imidazolium organic cations. They have exhibited high activity and good selectivity for target methoxy diphenyl methane in the benzylation of anisole with benzyl alcohol. It is noteworthy that the obtained solid hybrid catalysts are dissolved in the system at reaction temperature, but appear in the solid state again after cooling. This environmentally benign “liquid-phase reaction at high temperature, solid-state separation at room temperature” performance, which can be due to the structural feature of organic-heteropolyacid hybrid ionic liquids, enables an easy recovery and quite steady reusability of hybrids demonstrated by a three-run recycling test.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.07.039.

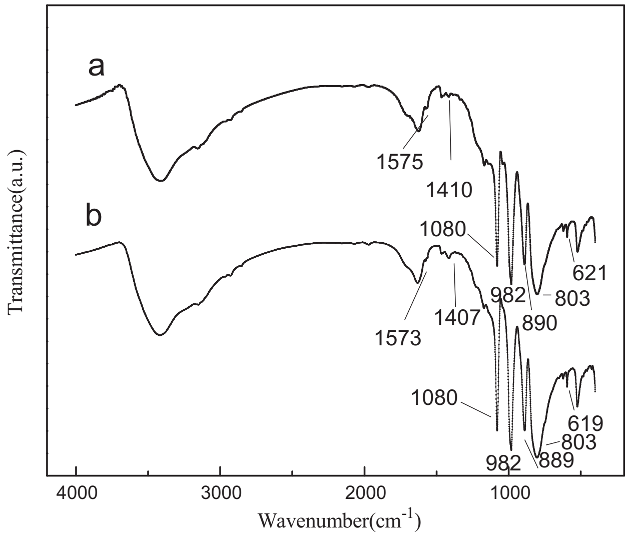

Fig. 3. FT-IR spectra for $H_2[MIMPS]PW_{12}O_{40}$. (a) Before use (b) after use.

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