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$[Hmim]_3PW_{12}O_{40}$: A high-efficient and green catalyst for the acetalization of carbonyl compounds

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Abstract

$[Hmim]_3PW_{12}O_{40}$ was developed and used in the acetalization of carbonyl compounds in excellent yields. The ionic liquid-heteropoly acid hybrid compound and reaction medium formed temperature-dependent phase-separation system with the ease of product as well as catalyst separation. The catalyst was recycled more than 10 times without any apparent loss of catalytic activity.

Keywords: $[Hmim]_3PW_{12}O_{40}$; Phosphotungstic acid; Carbonyl compounds; Acetalization; Ionic liquid

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Acetalization plays an important role in organic synthesis for the protection of carbonyl groups [1], and usually is achieved by treatment of carbonyl compounds with an alcohol or diol in the presence of Brønsted or Lewis acids [2]. However, those procedures own some drawbacks such as many by-products and serious environmental pollution. Besides that, the separation of the products from the catalytic system is also difficult.

Recently, heteropoly acids (HPAs) especially Keggin type have attracted increasing interest due to their high acidity, low toxicity and tunable redox properties [3]. Unfortunately, most HPAs exhibit some difficulties for product separation in homogeneous catalytic systems. The deposition of HPAs on porous solid supports has been considered as an effective means for improving properties and obtaining better performance in many potential heterogeneous catalytic applications [4]. However, HPAs supported on carrier by physisorption still show a degree of solubility in the reaction medium, which causes low recovery ratio and difficulty of separation. Thus, to develop novel HPAs and their salts is a crucial task at present.

Ionic liquids (ILs) absorbed more and more interests of researchers and successfully used in acetalization reaction due to low corrosion tendencies, good thermal stability and reusage [5]. In view of the advantages of ILs and HPAs, the ionic liquid based hybrid molecular materials have been studied [6]. Some researchers have already reported IL–solid catalytic systems. However, these ILs inevitably showed some drawbacks such as low recovery ratio, low yield or difficulty of synthesis. In addition, they were used as electrochemical rather than as catalysts. Herein, we report a Keggin phosphotungstate anion based Brønsted acidic ionic salt $[Hmim]_3PW_{12}O_{40}$ could be used as a high-efficient, reusable and environmental-friendly catalyst for the acetalization of carbonyl compounds (Scheme 1).

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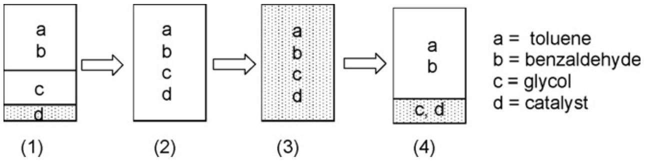

Scheme 1.

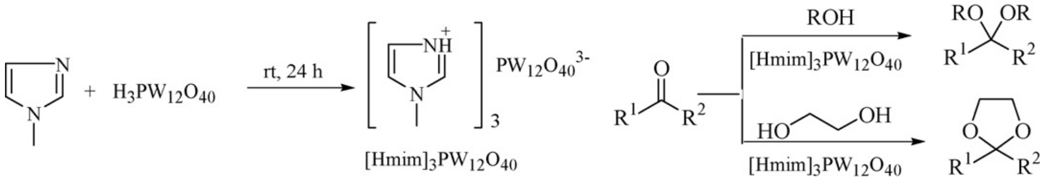

Fig. 1. Illustration of the acetalization of benzaldehyde with glycol using $[Hmim]_3PW_{12}O_{40}$ as catalyst: (1) heterogeneous mixture before the reaction at room temperature; (2) homogeneous mixture during the reaction at reflux; (3) near completion of the reaction; and (4) at the end of the reaction at room temperature.

1. Results and discussion

$[Hmim]_3PW_{12}O_{40}$ was obtained from phosphotungstic acid and *N*-methyl imidazole with 95% yield at room temperature [7]. It is white solid with high melting point (>300 °C), which is absolutely different from conventional ionic liquids. $[Hmim]_3PW_{12}O_{40}$ can be dissolved in dimethyl sulfoxide, however, it does not dissolve readily in other standard organic solvents and water at room temperature. The unique property is coincident with the requirements of a solid catalyst.

To study the catalytic activity of $[Hmim]_3PW_{12}O_{40}$, the acetalization of benzaldehyde and glycol was chosen as reaction model. The reaction was performed smoothly and 2-phenyl-1,3-dioxolane was obtained with 97% yield [8]. It may be mentioned here that the catalyst and reaction medium formed temperature-dependent phase-separation system in the acetalization of benzaldehyde (Fig. 1). The outstanding feature of the catalyst is that it scarcely dissolves in standard organic solvents and water at room temperature, but can dissolve in glycol at high temperature due to the formation of H-bonding between $[Hmim]_3PW_{12}O_{40}$ and glycol. Thus, the reaction system was heterogeneous at room temperature and then became homogeneous at reflux during the reaction. As the consumption of glycol, the system became heterogeneous and induced a spontaneous self-separation of the catalyst. The unusual behavior was also observed in the acetalization of other carbonyls and glycol.

Because glycol was one of the reactants, the catalyst layer was recycle used without any further purification. Performance of recycling used $[Hmim]_3PW_{12}O_{40}$ was investigated in the reaction of benzaldehyde with glycol. As shown in Table 1, $[Hmim]_3PW_{12}O_{40}$ could be easily recycled and reused 10 times without obvious loss of activity. Moreover, the recovery yield of the catalyst was obtained more than 93% after reused 10 times.

In order to prove the merits of the catalyst in the present work, we compared the catalytic activity of $[Hmim]_3PW_{12}O_{40}$ with other catalysts reported previously, and the data were listed in Table 2. Although inorganic salts and Brønsted acids could catalyze the acetalization reaction, the yields were dissatisfactory (Table 2, entries 1–4). Moreover, some of these catalysts are not stable in air. In cases of I_2, $H_4SiW_{12}O_{40}$, $H_3PW_{12}O_{40}$/Pan and $H_3PW_{12}O_{40}$, due to their shortcomings of difficult recovery and too many by-products, they could not be considered as economic and green catalysts even though some of them displayed good catalytic capacity. As for $[TMPSA]HSO_4$,

Table 1
The recycle of $[Hmim]_3PW_{12}O_{40}$.

Cycles	1	2	3	4	5	6	7	8	9	10
Yields[a]	97	98	97	96	95	94	93	93	92	92

[a] Chemical yields of the reaction.

Table 2
Comparison of the effect of catalysts in acetalization of benzaldehyde with glycol.

Entry	Catalyst	Yield (%)
1	$FeCl_3 \cdot 6H_2O$	58 [2g]
2	H_2NSO_3H	43 [2a]
3	$Bi(OTf)_3 \cdot 4H_2O$	73 [2c]
4	Al-SBA-15	65 [2f]
5	I_2	92 [2h]
6	$H_4SiW_{12}O_{40}$	84 [2g]
7	$H_3PW_{12}O_{40}$/PAn	76 [2i]
8	IL-1000/TsOH	92 [2j]
9	[TMPSA]HSO_4	77 [2k]
10	[PSebim]HSO_4	72 [2d]
11	$H_3PW_{12}O_{40}$	68
12	[Hmim]$_3PW_{12}O_{40}$	97

Reaction conditions: benzaldehyde (50 mmol), glycol (75 mmol), catalyst (0.44 mmol), toluene (8 mL), reflux for 2 h.

[PSebim]HSO_4 and IL-1000/TsOH, they gave the desired products in moderate to excellent yields, however, these catalysts are expensive and require special efforts for preparation. [Hmim]$_3PW_{12}O_{40}$ could be easily recycled and reused 10 times without obvious loss of activity and weight. Thus, in view of excellent catalytic capacity, low cost, outstanding stability and ready reutilization, [Hmim]$_3PW_{12}O_{40}$ was chosen as an effective catalyst for acetalization reaction of benzaldehyde and glycol.

In order to evaluate the generality of the process, we extended experiments to a series of alcohols and carbonyl compounds. The reaction proceeded smoothly. Corresponding acetals and ketals were obtained in high yields in most cases (Table 3). Due to its unique structure with two active sites, glycol usually reacts more actively than monohydroxy alcohol. The yields of acetalization of glycol and benzaldehydes vary depending upon the types and positions of substitutions. The results showed that the electron-donating groups decrease the yield, whereas electron-withdrawing groups increase it. Due to steric factors, *o*-hydroxybenzaldehyde reacted more slowly than *p*-hydroxybenzaldehyde.

Table 3
Acetalization of carbonyl compounds.

Entry	Carbonyl compounds		Alcohol	Time (h)	Yield (%)[a]
	R^1	R^2			
1[b]	C_6H_5–	H–	Methanol	2	82
2[b]	C_6H_5–	H–	Ethanol	2	79
3[b]	C_6H_5–	H–	Butan-1-ol	3	81
4[c]	C_6H_5–	H–	Glycol	2	97
5[c]	C_2H_5–	H–	Glycol	2.5	99
6[c]	C_3H_7–	H–	Glycol	2.5	96
7[c]	*iso*-C_4H_9–	H–	Glycol	3	93
8[c]	4-OH–C_6H_5–	H–	Glycol	4	78
9[c]	3-OH–C_6H_5–	H–	Glycol	4	85
10[c]	2-OH–C_6H_5–	H–	Glycol	6	62
11[c]	4-NO_2–C_6H_5–	H–	Glycol	1.5	97
12[c]	3-NO_2–C_6H_5–	H–	Glycol	1.5	96
13[c]	2-NO_2–C_6H_5–	H–	Glycol	4	88
14[c]	4-Cl–C_6H_5–	H–	Glycol	1.5	95
15[c]	3-Cl–C_6H_5–	H–	Glycol	1.5	94
16[c]	C_6H_5–	CH_3–	Glycol	5	89
17[c]	–C_4H_6–	–CH_2–	Glycol	2	98
18[c]	C_2H_5–	CH_3–	Glycol	3.5	90

Reaction conditions: carbonyl compound (50 mmol), alcohol ([b]150 mmol; [c]75 mmol), toluene (8 mL), [Hmim]$_3PW_{12}O_{40}$ (0.44 mmol), reflux.

[a] Detected by GC/MS. Yields were based on the starting carbonyl compounds.

Because alkyl group provides more electron density and steric crowding, acetophenone has a lower reactivity than benzaldehyde.

2. Conclusion

In conclusion, $[Hmim]_3PW_{12}O_{40}$ was facilely prepared and used as a high-efficient catalyst for the acetalization of carbonyl compounds. $[Hmim]_3PW_{12}O_{40}$ has several advantages: (1) it and reaction medium can form temperature-dependent phase-separation system with the ease of product as well as catalyst separation; (2) it was recycled more than 10 times without any apparent loss of weight and catalytic activity; (3) it has a wide range of application for different substrates and the products can be obtained conveniently in good to high yields. In a word, $[Hmim]_3PW_{12}O_{40}$ is an excellent reusable catalyst.

Acknowledgments

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[7] Phosphotungstic acid (5 mmol) and deionized water (15 mL) was added drop wisely into *N*-methyl imidazole (15 mmol) in 30 min with constant stirring. Then the materials were stirred at room temperature for 24 h. Finally, the produced white solid was filtrated, washed and dried (95% yield). Mp > 300 °C; IR (KBr): ν (cm^{-1}) 3330, 3159, 2871, 1585, 1548, 1438, 1384, 1330, 1151, 1080, 979, 893, 808, 740, 622, 592; ^1H NMR (300 MHz, DMSO-d_6, TMS): δ 3.85 (s, 3H, CH_3), 7.60 (s, 1H, CH), 7.65 (s, 1H, CH), 8.92 (s, 3H, CH); Anal. Calcd. for $C_{12}H_{21}N_6PW_{12}O_{40}$: C 4.61, H 0.68, N 2.69, P 0.97, W 68.76; found C 4.59, H 0.71, N 2.68, P 0.98, W 68.73; ESI-MS (energy: 50v, *m*/*z*, *z* = 3): 958.3 (48%), 701.5 (100%), 470.6 (41%).

[8] Representative procedure: the mixture of benzaldehyde (50 mmol), glycol (75 mmol), toluene (8 mL) and $[Hmim]_3PW_{12}O_{40}$ (0.44 mmol) was stirred at 80 °C for certain time. Water formed in the process was removed by azeotropic distillation using toluene as water-taken reagent. After the reaction, the organic layer was separated by decantation, and the product was detected by GC–MS (GC yield: 97%). The catalyst was reused without any treatment.