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Short Communication

Polyoxometalate-based acid salts with tunable separation properties as recyclable Brönsted acid catalysts for the synthesis of β-keto enol ethers

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ABSTRACT

Various polyoxometalate-based acid salts were synthesized by combining Keggin anions with sulfonated ammonium, imidazolium and pyridinium cations and used as catalyst for the synthesis of β-keto enol ethers. The sulfonated pyridinium cation with $SiW_{12}O_{40}^{4-}$ anion ($[PyPS]_4SiW$), showed the best activity and recyclability. Depending on the polarity of reaction mixture, "self-separation" or heterogeneous catalysis was observed. The catalyst was conveniently separated from the products, easily recycled and reused several times without significant loss of its activity.

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1. Introduction

In the last decade, the application of ionic liquids (ILs) in catalysis has been the subject of intensive research in academia and industry because of their adjustable physical and chemical properties [1–3]. Recent trends in the field of IL chemistry are the catalytic applications of the so-called "task-specific ILs" which were prepared by incorporating a functional group responsible for catalysis in their ionic partners [4,5]. Through the different combination of positive and negative ions, different hybrid materials can be designed and synthesized [6,7]. An interesting example of organic–inorganic hybrid materials was first reported by Leng et al. [8]. The combination of propane sulfonate functionalized organic cations with Keggin type polyoxometalate led to the formation of polyoxometalate-based acid salts that possesses unique structural and physicochemical properties. They were used as "reaction-induced self-separation catalysts" for various esterification reactions with one of the reactants being polycarboxylic acid or polyol [8]. As far as we know, the applications of these hybrid materials as "reaction-induced self-separation catalysts" are limited to esterifications and transesterification of trimethylolpropane [8–10]. In view of the emerging importance of polyoxometalate-based acid salts as novel, clean and recyclable catalyst [11,12], extending their applications in various organic transformations can be of considerable interest.

Among the different protocols for the synthesis of useful building blocks, we selected the synthesis of β-keto enol ethers because of their very high impact as synthons for the preparation of bioactive compounds, terpenoids, 4-alkylated-2-cyclohexenones, 2-aryl and 2-alkenyl-3-alkoxycyclohexenones and bicyclo [2,2,2] octenones [13–15]. Also, they act as dienophiles in Diels–Alder reactions [16]. However, the synthesis of β-keto enol ethers has received little attention despite their wide range of applications [17–21] and developing a new, cost-effective and green protocol for this transformation is still a challenging task.

In this study, we reported our efforts at extending the application of polyoxometalate-based acid salts as "self-separation" catalysts in the synthesis of β-keto enol ethers.

2. Experimental

2.1. Preparation of catalysts

The catalysts (Fig. 1) were synthesized according to previous literature [8]. For the synthesis of $[PyPS]_3PW$ catalyst, pyridine (0.11 mol) and 1,3-propanesultone (0.10 mol) were dissolved in toluene (30 mL) and stirred at 40 °C for 24 h under nitrogen atmosphere. A white precipitate (PyPS) was formed. It was filtered, washed with diethyl ether three times and dried in vacuum. PyPS (0.06 mol) was added to an aqueous solution of $H_3PW_{12}O_{40}$ (PW) (0.02 mol), and then the mixture was stirred at room temperature for 24 h. Water was removed in vacuum to give the final product as a solid. Other catalysts were prepared accordingly. IR and ^1H NMR data, elemental analyses and melting points of the catalysts are given in the supplementary information.

2.2. Catalytic reaction

The catalyst (0.2 g) was added to a solution of β-diketone (1 mmol) in alcohol (4 mL). The mixture was stirred at 50 °C. After

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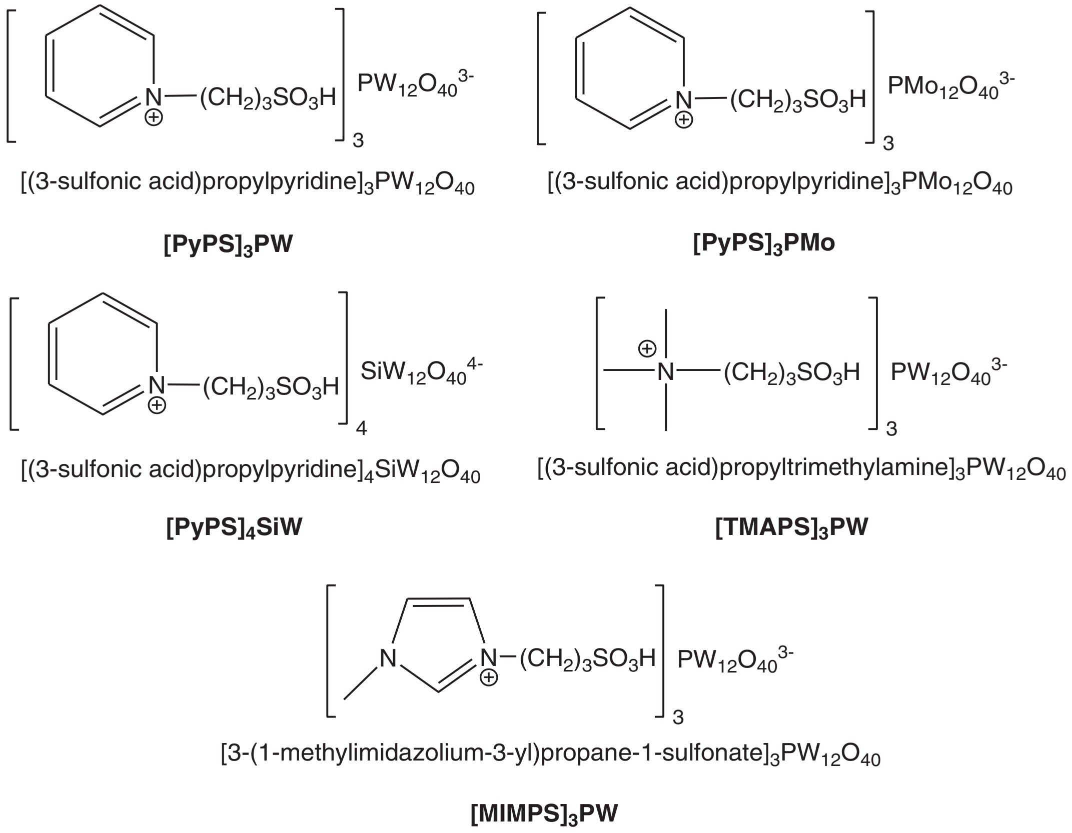


Fig. 1. Structures of various catalysts used in this study.

completion of the reaction, the catalyst was separated by decantation (or filtration). The filtrate was concentrated to generate the crude product. The crude products were purified by column chromatography on silica gel using hexane/EtOAc (4:1) as eluent. All products were characterized by ^{1}H NMR and IR spectroscopy.

3. Results and discussion

Acidity and solubility of polyoxometalate-based acid salts are major factors that should be considered in their catalytic applications. These factors have significantly affected by the choice of organic cations and/or inorganic anions. The acidity of HPAs is often discussed in terms of numbers and strength of acidic sites. These parameters can be estimated by potentiometric titration with n-butylamine [22]. However, the Brönsted acidity of ILs was usually determined by the Hammett acidity function (H_0). Up to now, there was no report in the literature to determine the acidity of polyoxometalate-based acid salts by potentiometric titration with n-butylamine. Therefore, the Brönsted acidity of the catalysts was determined by the Hammett method (see supplementary information). For comparison purposes, the number and strength of acid sites were estimated by potentiometric titration (for more details please see supplementary information). According to H_0, all of the catalysts have strong acidity (Table 1). Potentiometric titration curves obtained for different catalysts are presented in Fig. 2. As a criterion to interpret the obtained results, it was suggested that the initial electrode potential (Ei) indicates the maximum acid strength of the sites. The value of mmol amine/g catalyst, where the plateau is reached, indicates the total number of acid sites. All catalysts present very strong acidity and the same number of acidic sites.

The solubility of the catalysts was investigated in the model reaction (Scheme 1) at different temperatures. All catalysts were insoluble in methanol at room temperature. When 1 mmol of 5,5-dimethylcyclohexan-1,3-dione (dimedone) was added, $[MIMPS]_3PW$ and $[TMAPS]_3PW$ catalysts started to be dissolve. The system became

Table 1
Effect of organic cations in the acidity of hybrid catalysts.

Catalyst	A_{max}	[I] (%)	[IH$^+$] (%)	H_0[a]
–	1.496	100	0	–
$[TMAPS]_3PW$	0.79	52.8	47.2	1.03
$[MIMPS]_3PW$	0.70	47.0	53.0	0.94
$[PyPS]_3PW$	0.77	51.5	48.5	1.01
$[PyPS]_4SiW$	0.82	54.8	45.2	1.07
$[PyPS]_3PMo$	0.85	56.8	43.2	1.10

[a] $H_0 = pK_a + \log[I]/[IH^+]$; indicator: 4-nitroaniline ($pK_a = 0.99$); concentration of POM-IL: 0.1 mmol/L; concentration of 4-nitroaniline: 2 mmol/L.

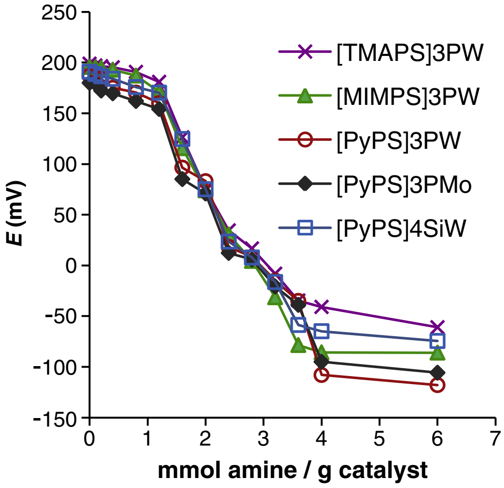
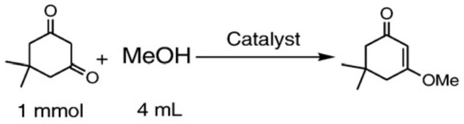


Fig. 2. Potentiometric titration curves.



Scheme 1. Model reaction.

clear gradually with heating continually, and these catalysts were dissolved completely at 50 °C. However, $[PyPS]_3PW$ catalyst remained insoluble at room temperature and its solubility was partially increased at 50 °C.

Considering that the catalysts were insoluble in the reaction medium at room temperature, the model reaction was carried out at 50 °C (Table 2). Control experiment showed that the substrates hardly reacted in the absence of catalyst (entry 1). For the hybrid catalysts with the same anion groups, the change of cations has little influence on the catalytic activity (entries 2–4). But solubility of the catalysts has significantly changed. At the beginning of the reaction, $[MIMPS]_3PW$ and $[TMAPS]_3PW$ catalysts, were dissolved in the reaction medium to form a homogeneous mixture. With the consumption of dimedone during the reaction, the system became turbid and the catalyst was precipitated at the end of the reaction (entries 2, 3). In the case of $[PyPS]_3PW$ catalyst, the cloudy mixture at the beginning of the reaction became heterogeneous with the consumption of dimedone (entry 4). These catalysts were separated from the reaction mixture, dried in vacuum and weighed. The wt.% of precipitated catalysts was increased in the following order: $[PyPS]_3PW > [TMAPS]_3PW > [MIMPS]_3PW$ (entries 2–4). Therefore, PyPS was selected as the best cation for the preparation of polyoxometalate-based acid salts. The influence of various HPAs in the activity and solubility of catalysts with the same PyPS cation is shown in entries 4–6. $[PyPS]_4SiW$ showed the best recyclability and 96 wt.% of the catalyst was precipitated at the end of the reaction (entry 6). The catalytic activity of various hybrid catalysts was compared with counterpart cations and HPAs (Table 2). The results showed that the counterpart cations TMAPS and PyPS were insoluble in the reactants and/or products, and the yields of products were lower than those obtained using hybrid catalysts (entries 7, 8). However, when MIMPS was used as catalyst, a homogeneous system resulted which gave a moderate yield of the product (entry 9). The product was obtained in good yields by using the pure HPAs. But, the reaction proceeded in a homogeneous system with difficult catalyst recovery (entries10–12).

The model reaction was carried out in the presence of different amounts of $[PyPS]_4SiW$ as the best catalyst (Fig. 3). Excellent yield of the product was obtained when only 0.2 g of $[PyPS]_4SiW$ was used. The use of higher amounts of the catalyst had no significant effect in the product yield (it should be noted that catalyst solubility was not changed with increasing the amount of the catalyst even to 0.25 g).

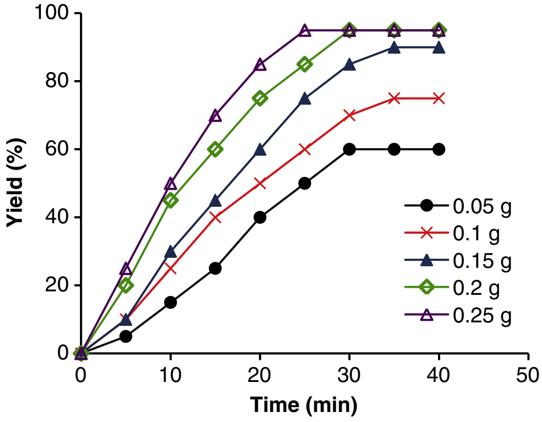


Fig. 3. Effect of catalyst loading in the model reaction.

Table 2
Efficacies of various catalysts in the model reaction.[a]

Entry	Catalyst (g)	Reaction phenomenon	Recyclability (wt.%)	Time (min)	Yield (%)[b]
1	–	–	–	180	10
2	$[TMAPS]_3PW$	Phase separation	42	45	98
3	$[MIMPS]_3PW$	Phase separation	36	45	98
4	$[PyPS]_3PW$	Phase separation	78	45	90
5	$[PyPS]_4SiW$	Phase separation	96	45	87
6	$[PyPS]_3PMo$	Homogeneous	–	45	82
7	TMAPS	Heterogeneous	–	90	31
8	PyPS	Heterogeneous	–	90	15
9	MIMPS	Homogeneous	–	90	66
10	PW	Homogeneous	–	30	91
11	PMo	Homogeneous	–	30	84
12	SiW	Homogeneous	–	30	89

[a] Reaction condition: dimedone (1 mmol), methanol (4 mL), catalyst (0.1 g), 50 °C.
[b] Isolated yield.

Catalytic reusability of $[PyPS]_4SiW$ without any regeneration steps was investigated in the model reaction (Fig. 4). At the fourth reaction run, 87.5 wt.% of the catalyst (compared with the amount of fresh one used in the first run) was recovered (see supplementary information) and yield of the product decreased from 95% to 83%. This decrease in the product yield may be due to the weight loss in the operation for recovering and/or deactivation of the catalyst. In order to find which one is the main reason for decreasing the product yield, a control test was performed using the same amount of fresh catalyst ($0.2 \times 87.5\% = 0.175$ g) and 88% yield of the product was obtained. Therefore, taking into account the weight loss in the operation for the recovering of the catalyst, only 5% decrease in the product yield is due to very slow catalyst deactivation. In light of this, $[PyPS]_4SiW$ catalyst showed excellent reusability and self-separation performance during the four cycles.

To evaluate the scope of the $[PyPS]_4SiW$ as “self-separation catalyst” for the synthesis of β-keto enol ethers, different alcohols were used as reactants (Table 3). Methyl, primary, and secondary alcohols, reacted with dimedone without any significant difference to give the corresponding products in good to excellent yields. tert-Butanol was also reacted with dimedone to provide the corresponding β-keto enol ether in 30% yield (entry 8), while some previous approaches did not apply this alcohol or gave negative results for similar reactions [17–21].

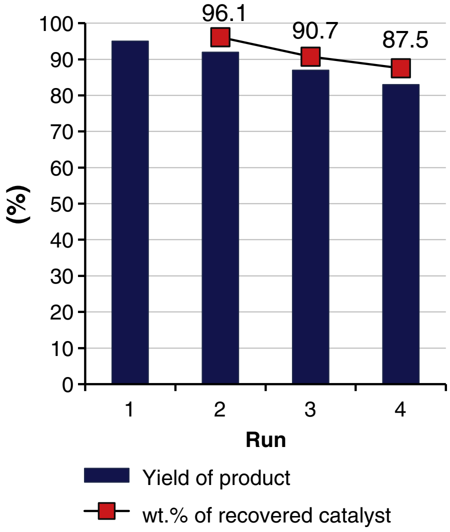
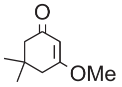
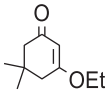
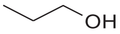
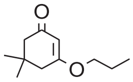
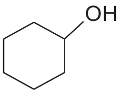
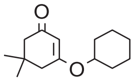
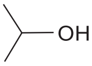
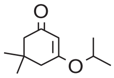
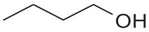
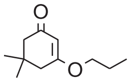
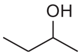
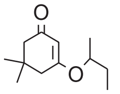
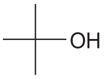
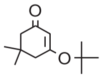


Fig. 4. Catalytic reusability in the model reaction (after 30 min).

Table 3
Synthesis of β-keto enol ethers using $[PyPS]_4SiW$ catalyst.[a]

Entry	Alcohol	Product	Reaction phenomenon	Time (min)	Yield (%)[b]
1	MeOH		Phase separation	30	95
2	EtOH		Phase separation	40	84
3			Phase separation	47	91
4			Phase separation	95	86
5[c]			Heterogeneous	90 (110)	80 (81)
6[c]			Heterogeneous	45 (60)	96 (94)
7[c]			Heterogeneous	70 (80)	91 (88)
8[c]			Heterogeneous	100 (120)	30 (27)

[a] Reaction condition: diketone (1 mmol), alcohol (4 mL), catalyst (0.2 g), 50 °C.
[b] Isolated yields.
[c] Reaction condition: diketone (3 mmol), alcohol (4 mL), catalyst (0.2 g), 50 °C, results in parenthesis.

Reaction phenomena varied with the catalyst's solubility in reactants containing different polar groups. The phase-separation behavior was observed in the cases of methanol, ethanol, propanol and cyclohexanol (entries 1–4) and the reaction medium switched from a homogeneous system to heterogeneous one at the end of the reactions. In these cases, the phase transfer catalysis combined the advantages of both homogeneous and heterogeneous systems. The other entries were heterogeneous systems (entries 5–8). In order to increase the catalyst's solubility, the excess amount of dimedone was used in these reactions. In all cases, the catalyst remained insoluble and reaction times were significantly increased (entries 5–8, results in parenthesis). However, high yields were also obtained in these heterogeneous systems possibly because of the pseudo-liquid phase behavior of polyoxometalate-based acid salts [11].

4. Conclusion

The main findings of this work can be summarized as follows:

1. The changes of cations and HPAs have little influence on the catalytic activity of polyoxometalate-based acid salts but their solubilities have significantly changed.
2. $[PyPS]_4SiW$ showed the best recyclability and excellent catalytic activity.
3. Reaction phenomena varied with the catalyst's solubility in reactants containing different polar groups. Depending on the polarity of reaction mixture, “self-separation” or heterogeneous catalysis was observed.
4. The catalyst was conveniently separated from the products, easily recycled and reused several times without significant loss of its activity.

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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.2012.04.009.

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