Acid catalysis of different supported heteropoly acids for a one-pot synthesis of β-acetamido ketones

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Abstract

The production of β-acetamido ketones from aldehydes, ketones and acetyl chloride in acetonitrile over supported heteropoly acids has been examined. This study reports the use of heteropoly acids (HPAs) supported on metal oxides (SiO_2, Al_2O_3, K 10 and KSF montmorillonite) and activated carbon as efficient and reusable catalysts, and their comparison with other catalysts in Dakin–West reaction. Dodecatungstophosphoric acid supported on KSF and γ-Al_2O_3 shows the best results and reusability.
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Keywords: Dakin–West reaction; Heterogeneous catalyst; Supported heteropoly acid; Multi-component reaction; β-Acetamido ketone

1. Introduction

In the last decade, HPAs have attracted great interest of catalyst researchers. Their acid–base and redox properties are widely used in heterogeneous catalysis [1–3]. Heteropoly compounds with Keggin structure are the most studied in the polyoxometalate class because they possess relatively high thermal stability and high intrinsic acidity [4,5]. HPAs have low specific surface area (1–$10 \, m^2/g$). It is important to increase the surface area or even better to increase the number of accessible acid sites of the HPAs. This can be achieved by dispersing the HPAs on solid supports with high surface area [6–8]. Surface area enhancement, higher dispersion of acidic protons, heterogenization and acid strength control are some of the goals of using supported HPAs. These supported catalysts are widely studied and found useful in many reactions such as the synthesis of 2,4-dihydropyrimidones [9], the synthesis of α-aminonitriles [10], esterification [11,12], the synthesis of metanethole [13], etc.

Multi-component reactions (MCRs) are of increasing importance in organic and medicinal chemistry for various reasons [14–16]. In times when a premium is put on speed, diversity, and efficiency in the drug discovery process [17], MCR strategies offer significant advantages over conventional linear-type syntheses. MCR condensations involve three or more compounds reacting in a single event, but consecutively, to form a new product, which contains the essential parts of all the starting materials. Therefore, search and discovery for new MCRs [18], along with full exploitation of the already known MCRs is of considerable interest. The Dakin–West reaction for the synthesis of β-acetamido ketones belongs in the latter category [19,20] (Scheme 1). These compounds are versatile intermediates, in that their skeletons exist in a number of biologically or pharmacologically important compounds [21,22]. $CoCl_2$ and montmorillonite K 10 clay [23,24] are found to be effective for the synthesis of β-acetamido ketones, but involve a long reaction time. Pandey et al. proposed another procedure for the condensation of aldehyde, acetophenone and acetyl chloride in the presence of Lewis acids, such as Zn (II), Bi (III), Sn (II), Sc (III), Cu (II) triflates, BF_3, $CuCl_2$, $BiCl_3$, $LaCl_3$, $LiClO_4$, $InCl_3$, and NiI, where $Cu(OTf)_2$ gave a high yield for this transformation [25]. A modified procedure for the Dakin–West reaction has been also reported using H_2SO_4/SiO_2 [26]. Recently the authors

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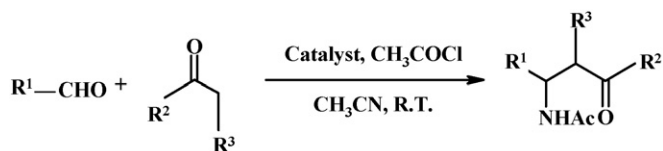
Scheme 1. Synthesis of β-acetamido ketones.

reported HPAs as highly efficient catalysts for the synthesis of β-acetamido ketones [27].

The aim of the present work is the comparison of activity of different supported HPAs for preparation of β-acetamido ketones.

2. Experimental

2.1. Techniques

Surface areas of HPA catalysts were measured by nitrogen physisorption on a Micromeritics ASAP 2000 instrument. FTIR spectra were recorded using a Bomem MB 104 spectrometer and IR spectra were recorded with KBr pellets using a Shimadzu 470 spectrophotometer. The tungsten content in the catalysts was measured by inductively coupled plasma (ICP) atomic emission spectroscopy on a Spectro Ciros CCd spectrometer. ^{1}H NMR spectra were recorded on a Bruker Avance 200 MHz NMR spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. The morphology of supported catalyst was studied by scanning electron microscopy (SEM) on a model XL30 Philips SEM.

2.2. Materials and catalysts

$H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$ hydrate from Aldrich, Merck and Aerosil 300 silica from Degussa were used. Carbon, KSF and K10 montmorillonite clay were obtained from Fluka. γ-Alumina was obtained from Aldrich.

2.3. Preparation of the catalysts

The catalysts were prepared using solutions of tungstophosphoric acid (PW), molybdophosphoric acid (PMo), or tungstosilicic acid (SiW). The solutions were used to impregnate supports with different characteristics. The solids employed as supports were Aerosil 300 silica (S_{BET}, 300 m^2/g), KSF and K 10 montmorillonites, activated carbon, and γ-Al$_2$O$_3$. The specific surface area of these supports is shown in Table 1, entries 1–5.

Silica-supported PW (PW/SiO$_2$) catalysts were prepared by impregnating Aerosil 300 silica (3.0 g) with an aqueous solution of PW (with concentrations depending upon the loadings, 20, 40 and 60 wt.% PW on silica). The mixture was stirred overnight at room temperature, followed by drying using a rotary evaporator, as described elsewhere [9].

For preparation of the PW/K 10, K 10 montmorillonite was dried in an oven at 120 °C for 2 h prior to its use as support. After drying, 5.0 g of K 10 was taken. To prepare a catalyst with

Table 1
Specific surface area of supports and supported PW

Entry	Catalyst	S_{BET}	Pore volume (cm^3/g)
1	SiO$_2$	311	1.7
2	K-10	200	0.36
3	KSF	15	–
4	Carbon	478	0.82
5	γ-Al$_2$O$_3$	250	0.67
6	20% PW/SiO$_2$	208	0.49
7	40% PW/SiO$_2$	117	0.36
8	60% PW/SiO$_2$	87	0.34
9	40% PW/K-10	82	0.27
10	40% PW/KSF	<5	–
11	40% PW/C	272	0.15
12	40% PW/γ-Al$_2$O$_3$	200	0.18

40% loading of PW, 2.0 g of PW was dissolved in 4 mL of dry methanol. This solution was added dropwise to predried K 10 with constant stirring with a glass rod. Initially with addition of PW solution, the clay was in the powdery form, but on further addition of PW solution, the clay turned to a paste form. The paste on further stirring for 10 min resulted in a free flowing powder. A similar procedure was followed for the synthesis of PW/KSF.

A catalyst based on PW supported on γ-Al$_2$O$_3$ was also prepared. The solution of PW was prepared by dissolving 2.0 g PW in 25 mL of water and 25 mL of methanol. Then 5.0 g γ-Al$_2$O$_3$ was dropped into the above solution under vigorous stirring to be impregnated for 24 h.

For preparation of PW/C, carbon was first subjected to an acid and base treatment to remove impurities. The catalyst was prepared by the pore filling impregnation technique with a PW solution. After the impregnation, all catalysts were dried at room temperature for 24 h, and calcined at 200 °C for 3 h.

2.4. Typical procedure for the synthesis of β-acetamido ketones

A solution of aldehyde (1 mmol), ketone (1 mmol), acetyl chloride (0.3 mL) and acetonitrile (3 mL) in the presence of an appropriate amount of catalyst was stirred at ambient temperature. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the filtrate was poured into 50 mL ice-water. The solid product was filtered, washed with ice-water and recrystallized from ethyl acetate/n-heptane to give the pure product. All products were identified by comparing their ^{1}H NMR and IR spectra with those of authentic samples [24,26,27].

3. Results and discussion

3.1. Characterization of the catalysts

The BET surface areas and pore volumes of various catalysts are listed in Table 1. Pure PW or PMo exhibited a very low surface area of <6 m^2/g. The surface area of supported catalysts decreased remarkably compared to their parent supports, but still

showed very high values. The reduction in the surface area of supported catalysts may be due to the blockage of smaller pores by active species.

The primary structures of supported HPAs were identified by comparing their FTIR absorption bands to those of bulk HPAs. Keggin PW consists of a PO_4 tetrahedron surrounded by four W_3O_{13} groups formed by edge-sharing octahedral. These groups are connected to each other by corner-sharing oxygens [28], and this arrangement gives rise to four types of oxygen bands between 1200 and 700 cm^{-1}, a fingerprint region for these compounds. Bulk PW shows the characteristic IR bands at *ca.* 1080 cm^{-1} (P−O in central tetrahedral), 985 cm^{-1} (terminal W=O), 890 and 814 cm^{-1} (W−O−W) associated with the asymmetric vibrations in the Keggin polyanions. It should be emphasized that some bands were overlapped with those of the supports. FTIR of the supported PW indicates that the primary Keggin structure is preserved after supporting PW on different supports (Fig. 1).

The SEM images of the gross morphology of some samples, supports, and the supported PW are displayed in Fig. 2 and show that the PW particles were randomly distributed over the support surfaces. It should be noted that the PW layer formed in all samples was constituted of several aggregates of PW particles and not by a continuous film.

3.2. Catalytic reaction

Since Keggin-type HPAs, e.g. PW, SiW, and PMo, were previously found to be highly active solid acid catalysts for Dakin–West reactions [27], the utilization of supported HPAs with different supports in the synthesis of β-acetamido ketones was studied. Ease of handling, good dispersion of active sites and the resulting improved reactivity, safer and milder reaction conditions, and reusability are a few advantages of using these supported reagents.

3.2.1. Efficacies of HPAs

At first the reaction of benzaldehyde, acetophenone and acetyl chloride in acetonitrile was performed in the presence of PW, PMo, and SiW (Table 2, entries 1–3). As expected [8], the results show that tungsten HPAs (PW, SiW) are preferred over molybdenum ones as acid catalysts, and PW – the strongest
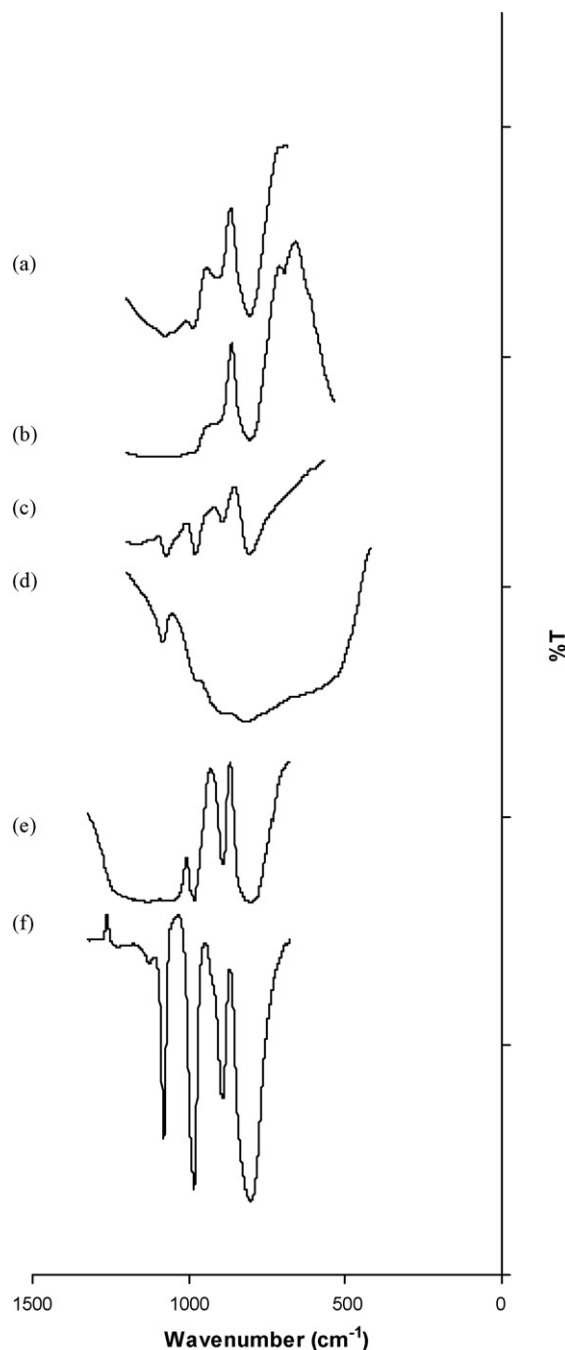

Fig. 1. FTIR spectra of (a) 40 wt.% PW/KSF; (b) 40 wt.% PW/K10; (c) 40 wt.% PW/C; (d) 40 wt.% PW/Al$_2$O$_3$; (e) 40 wt.% PW/SiO$_2$; (f) PW.

acid in the HPA series – is particularly recommended. Reactivity of different HPAs supported on KSF was also checked as a model system (Table 2, entries 4–6). PW/KSF caused the reaction efficiently compared with PMo/KSF, SiW/KSF, and KSF only (Fig. 3).

3.2.2. Efficacies of various catalysts

In this work the performance of several solid acid catalysts was evaluated for the synthesis of β-acetamido ketones. The efficacies of different catalysts are given in Table 3. In all the cases 40% (w/w) loading of PW over different supports was

Table 2
Efficacies of different HPAs in reaction of benzaldehyde, acetophenone, and acetyl chloride[a]

Entry	Catalyst	Time (min)	Yield (%)[b]
1	PW	75	95
2	PMo	100	88
3	SiW	100	92
4	40% PW/KSF	12	95
5	40% PMo/KSF	16	94
6	40% SiW/KSF	18	94

[a] Reaction condition: benzaldehyde:acetophenone, 1:1 mmol; acetyl chloride, 0.3 mL; solvent, acetonitrile, 3 mL; catalyst loading, 0.05 g/cm^3; room temperature.
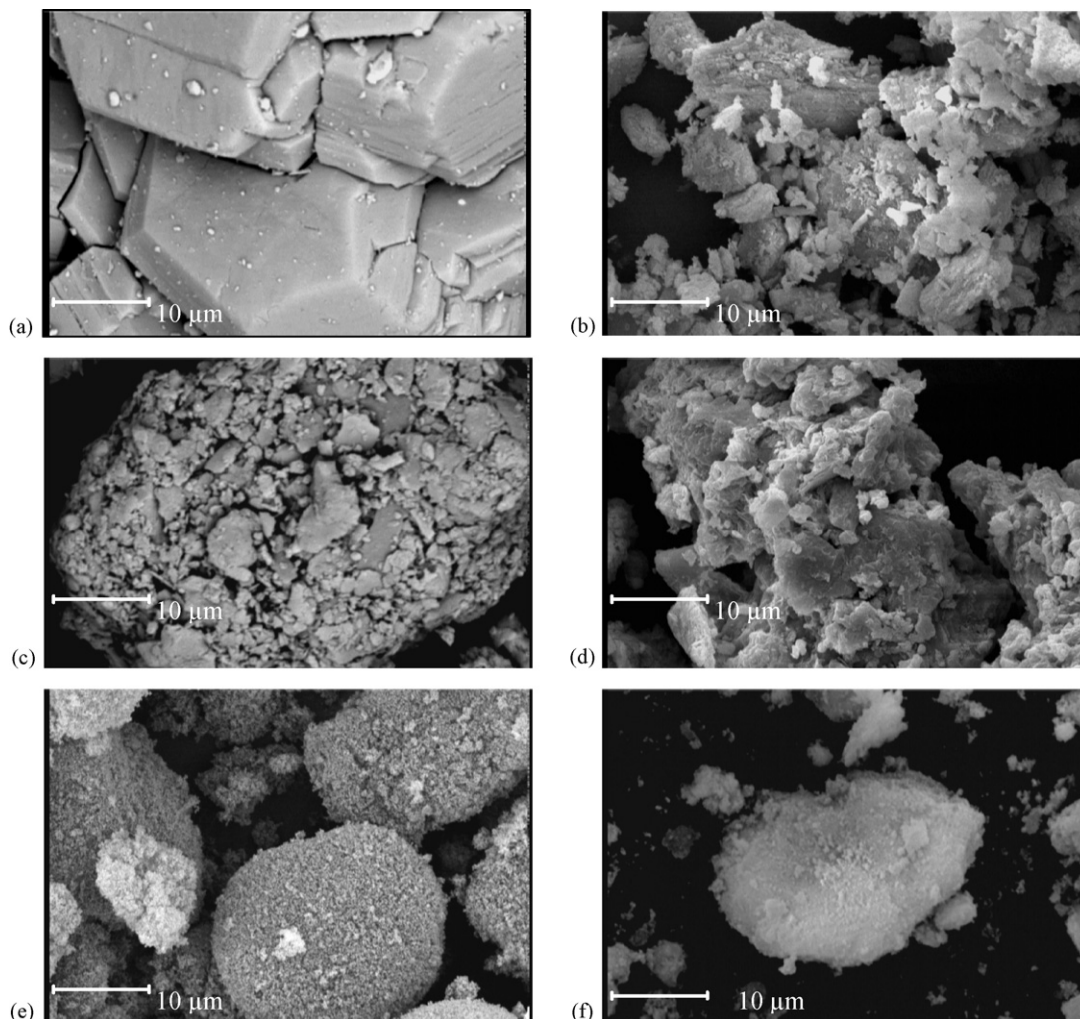[b] Isolated yield.

Fig. 2. SEM images of (a) Al$_2$O$_3$; (b) 40 wt.% PW/Al$_2$O$_3$; (c) KSF; (d) 40 wt.% PW/KSF; (e) SiO$_2$; (f) 40 wt.% PW/SiO$_2$; In all images EHT = 20 kV and ×1932.

found to be better than the support only on unit weight basis. β-Acetamido-β-(phenyl)propiophenone obtained by using PW supported on the five supports as a function of time is shown in Fig. 4. The support leads to a difference in the behavior of PW. When supported on γ-Al$_2$O$_3$, KSF or K 10 montmo-

rillonite, it allows reaching high conversion faster than other supports. Carbon-supported PW and silica-supported ones were less efficient than the other supported catalysts in the same reaction conditions. No significant difference was observed in the
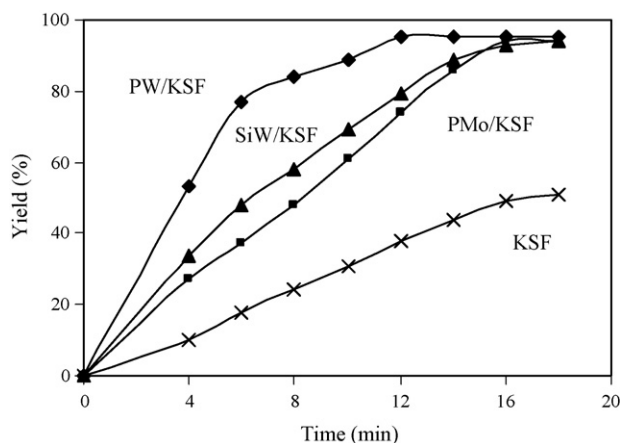

Fig. 3. Effect of different HPAs supported on KSF in the reaction of benzaldehyde, acetophenone, and acetyl chloride. Catalyst loading, 0.05 g/cm^3.

Table 3
Efficacies of various catalysts in reaction of benzaldehyde, acetophenone, and acetyl chloride[a]

Entry	Catalyst	Time (min)	Yield (%)[b]
1	SiO$_2$	60	4
2	K 10	60	20
3	KSF	30	60
4	Activated Carbon	100	10
5	γ-Al$_2$O$_3$	60	20
6	40% PW/SiO$_2$	60	67
7	40% PW/γ-Al$_2$O$_3$	10	93
8	40% PW/K 10	10	93
9	40% PW/KSF	12	95
10	40% PW/C	80	90

[a] Reaction condition: benzaldehyde:acetophenone, 1:1 mmol; acetyl chloride, 0.3 mL; solvent, acetonitrile, 3 mL; catalyst loading, 0.05 g/cm^3; room temperature.
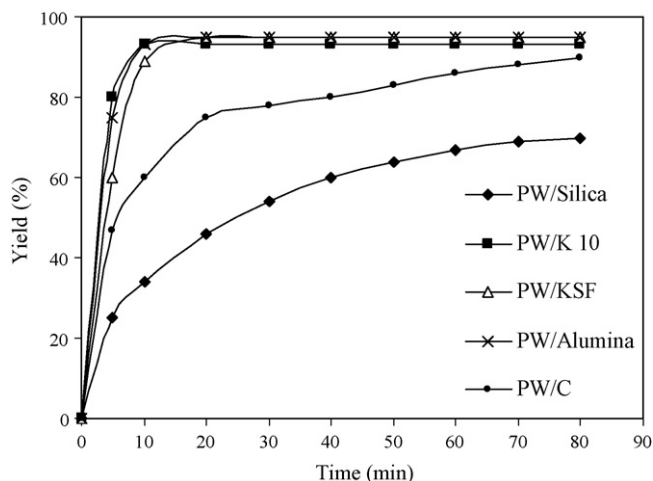
[b] Isolated yield.

Fig. 4. Effect of various supports in reaction of benzaldehyde, acetophenone, and acetyl chloride. Catalyst loading, 0.05 g/cm^3.

final yield of β-acetamido ketone (after 1 h) for all supported catalysts, except for PW/SiO$_2$.

3.2.3. Effect of PW loading on support

PW/SiO$_2$ was chosen as a model system to investigate the effect of different amounts of PW loading on support. Fig. 5 shows differences in catalytic activity among catalysts having 20, 40, and 60 wt.% of PW on silica. Lowering the loading of the deposited PW results in reduction of the catalytic activity. No improvements in the reaction rate and yield were observed by increasing the amount of PW on SiO$_2$ from 40 to 60 wt.%. Since 40 wt.% of PW/SiO$_2$ was the best catalyst loading, it was used to study the effect of various parameters on yields.

3.2.4. Effect of catalyst concentration

The catalyst concentration was varied over a range of 0.03–0.3 g/cm^3 on the basis of the total volume of the reaction mixture. Table 4 shows the effect of catalyst concentration on the reaction of benzaldehyde, acetophenone and acetyl chloride. On all the supports, the yield of the corresponding β-acetamido
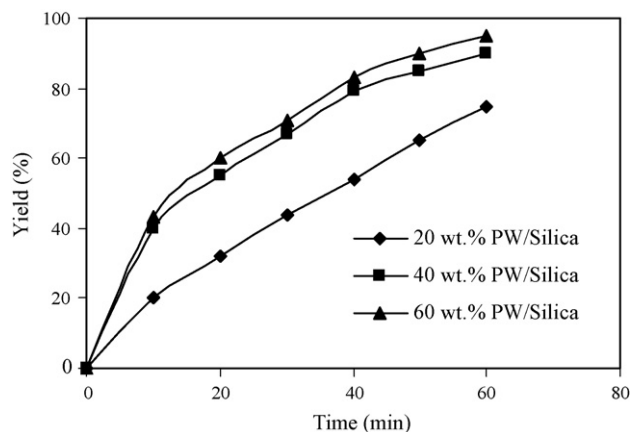

Fig. 5. Effect of percent of PW on SiO$_2$ in the reaction of benzaldehyde, acetophenone, and acetyl chloride. Catalyst loading, 0.3 g/cm^3.

Table 4
Effect of catalyst loading in the reaction of benzaldehyde, acetophenone, and acetyl chloride[a]

Entry	Catalyst	Catalyst loading (g/cm^3)	Time (min)	Yield (%)[b]
1	40% PW/SiO$_2$	0.05	60	67
2	40% PW/SiO$_2$	0.15	60	80
3	40% PW/SiO$_2$	0.3	60	90
4	40% PW/SiO$_2$	0.7	60	93
5	40% PW/γ-Al$_2$O$_3$	0.03	10	81
6	40% PW/γ-Al$_2$O$_3$	0.05	10	93
7	40% PW/γ-Al$_2$O$_3$	0.15	8	95
8	40% PW/γ-Al$_2$O$_3$	0.25	7	94
9	40% PW/K 10	0.03	10	79
10	40% PW/K 10	0.05	10	93
11	40% PW/K 10	0.15	7	95
12	40% PW/KSF	0.03	12	84
13	40% PW/KSF	0.05	12	95
14	40% PW/KSF	0.15	12	96
15	40% PW/C	0.03	90	83
16	40% PW/C	0.05	80	90
17	40% PW/C	0.07	60	95
18	40% PW/C	0.15	50	94

[a] Reaction condition: benzaldehyde:acetophenone, 1:1 mmol; acetyl chloride, 0.3 mL; solvent, acetonitrile, 3 mL; room temperature.
[b] Isolated yield.

ketone increased with increasing catalyst concentration on the PW.

Rate of the reaction was slow with PW/SiO$_2$ and PW/C compared to PW/γ-Al$_2$O$_3$, PW/K 10 or PW/KSF in the same reaction conditions (Fig. 4 and Table 4). The yield of the product markedly changed with catalyst concentrations up to 0.3, 0.07, 0.05, 0.05, and 0.05 g/cm^3 of 40 wt.% of PW/SiO$_2$, PW/C, PW/γ-Al$_2$O$_3$, PW/K 10, and PW/KSF, respectively (Table 4). Further addition of catalyst had no noticeable effect on the yield. This was due to the fact that beyond a certain concentration, there exist an excess of catalyst sites over what is actually required by the reactant molecules, and hence, the additional catalyst does not increase the rate of the reaction. Therefore, in all further reactions 0.3, 0.07, 0.05, 0.05, and 0.05 g/cm^3 were used for 40 wt.% of PW/SiO$_2$, PW/C, PW/Al$_2$O$_3$, PW/K 10, and PW/KSF, respectively.

3.2.5. Reusability of catalysts

Stability and reusability of a catalyst is a very important parameter before recommending any catalyst for industrial-scale use. To establish the reusability in reaction of benzaldehyde and acetophenone, 40 wt.% of PW were used four times on different supports (Table 5). After each run, the catalyst was recovered by filtering, thoroughly washed with acetonitrile and dried in an oven at 120 °C for 2 h, to remove the adsorbed reactants or product. When PW/K 10 was used, a significant decrease in yield was observed with its subsequent reuse, while this decrease was lighter when other supported catalysts were used repeatedly. A decrease in catalytic activity of 40 wt.% of PW/K 10 due to the leaching from the support was confirmed by a UV spectrum test of supernatant portion of the PW/K 10 catalyzed reaction mixture. A supernatant portion of the PW/K 10 catalyzed reaction

Table 5

Reusability of catalysts in reaction of benzaldehyde, acetophenone, and acetyl chloride[a]

Run no.	Time (min)/yield (%)[b,c]				
	PW/SiO$_2$	PW/K 10	PW/KSF	PW/γ-Al$_2$O$_3$	PW/C
1	60/90	10/93	12/95	10/93	60/95
2	60/80	10/56	12/92	10/86	60/89
3	60/72	10/51	12/87	10/80	60/84
4	60/67	10/50	12/85	10/75	60/77

[a] Reaction condition: benzaldehyde:acetophenone, 1:1 mmol; acetyl chloride, 0.3 mL; solvent, acetonitrile, 3 mL; room temperature.

[b] Isolated yield.

[c] Catalyst loading: PW/SiO$_2$, 0.3; PW/K 10, 0.05; PW/KSF, 0.05; PW/γ-Al$_2$O$_3$, 0.05; PW/C, 0.07 g/cm^3, respectively.

mixture exhibited an absorption band at around 265 nm assigned to Keggin-type PW$_{12}$O$_{40}^{3-}$ ions [29], whereas in other cases no such band was visible. FTIR spectra of fresh and used supported catalysts showed no change in the primary Keggin anion, even after their repeated use. It should be emphasized that both catalyst preparation and reaction conditions are mild. Thus it is reasonable that the Keggin unit should be intact under the reaction conditions. In the case of 40 wt.% of PW/SiO$_2$ as a model system, the reaction mixture was filtered 30 min after the first run. Then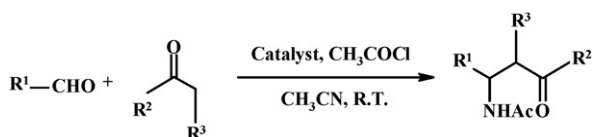 the reaction was resumed with the filtrate, in the absence of any externally added catalyst. No increase in conversion was observed after 2 h, which proves it is a real heterogenic catalyst.

3.2.6. Dakin–West reaction

The reaction was extended to other aryl and alkyl aldehydes and ketones as substrates under the optimum conditions for each catalyst (Table 6). The optimum amounts of catalysts for the preparation of β-acetamido ketones were 0.3, 0.07, 0.05, 0.05, and 0.05 g/cm^3 of PW/SiO$_2$, PW/C, PW/γ-Al$_2$O$_3$, PW/K 10, and PW/KSF, respectively. PW/K 10, PW/KSF, and PW/Al$_2$O$_3$ required shorter reaction times and lower catalyst loadings than PW/SiO$_2$ or PW/C. Aromatic aldehydes or acetophenones with either an electron-withdrawing or -donating substitutent afforded the β-acetamido ketones in excellent yields in relatively short reaction times at room temperature, without any formation of side products.

It is noteworthy that no acetylation of the aromatic hydroxyl group was observed when salicylaldehyde was used, and that the corresponding β-acetamido ketones were isolated in excellent yields (Table 6, entries 11–13). Aliphatic aldehyde and cyclic ketone gave unsatisfactory results at room temperature (Table 6, entries 16 and 18). The authors suggest a reaction mechanism that is shown in Scheme 2. The mechanism may involve α-chloroacetate from aldehyde and acetyl chloride. On further

Table 6

Synthesis of β-acetamido ketones at room temperature in the presence of different supported catalysts

Entry	R^1	R^2	R^3	Yield (%)[a,b]/time (min)				
				PW/SiO$_2$	PW/K 10	PW/KSF	PW/γ-Al$_2$O$_3$	PW/C
1	C$_6$H$_5$	C$_6$H$_5$	H	90/60	93/10	95/12	95/10	95/60
2	C$_6$H$_5$	4-NO$_2$C$_6$H$_4$	H	73/90	90/10	98/14	95/12	95/40
3	C$_6$H$_5$	4-BrC$_6$H$_4$	H	95/60	95/8	98/2	98/3	95/30
4	4-ClC$_6$H$_4$	C$_6$H$_5$	H	95/40	93/4	98/4	95/3	95/20
5	4-CH$_3$OC$_6$H$_4$	C$_6$H$_5$	H	80/90	92/10	97/8	90/7	98/30
6	2-ClC$_6$H$_4$	C$_6$H$_5$	H	90/60	91/18	98/12	94/10	95/60
7	4-CH$_3$C$_6$H$_4$	4-NO$_2$C$_6$H$_4$	H	96/60	85/12	90/12	95/12	93/60
8	4-ClC$_6$H$_4$	4-BrC$_6$H$_4$	H	95/70	98/4	98/8	90/5	97/20
9	4-ClC$_6$H$_4$	4-NO$_2$C$_6$H$_4$	H	92/60	86/6	85/14	94/15	95/30
10	4-CH$_3$OC$_6$H$_4$	4-NO$_2$C$_6$H$_4$	H	90/90	65/25	98/16	90/10	98/50
11	2-HOC$_6$H$_4$	C$_6$H$_5$	H	86/10	90/15	45/30	81/30	85/40
12	2-HOC$_6$H$_4$	4-NO$_2$C$_6$H$_4$	H	62/60	91/14	50/25	70/25	95/40
13	2-HOC$_6$H$_4$	4-BrC$_6$H$_4$	H	85/90	98/20	97/3[c]	85/50	95/40
14	3-NO$_2$C$_6$H$_4$	4-BrC$_6$H$_4$	H	95/60	90/6	95/8	95/10	98/30
15	3-NO$_2$C$_6$H$_4$	C$_6$H$_5$	H	91/70	95/12	98/4	95/5	95/40
16	CH$_3$CH$_2$	C$_6$H$_5$	H	10/240	15/60	12/60	30/80	10/60
17	CH$_3$CH$_2$	C$_6$H$_5$	H	82/60[c]	75/6[c]	40/25[c]	70/5[c]	85/25[c]
18	C$_6$H$_5$	C$_6$H$_{10}$O		41/240	12/60	50/16	5/50	10/60
19	C$_6$H$_5$	C$_6$H$_{10}$O		85/60[c]	84/10[c]	80/10[c]	93/8[c]	92/70[c]

[a] Isolated yield, all products were identified by comparing their NMR and IR values with those for authentic samples [27].

[b] Catalyst loading: PW/SiO$_2$, 0.3; PW/K 10, 0.05; PW/KSF, 0.05; PW/γ-Al$_2$O$_3$, 0.05; PW/C, 0.07 g/cm^3.

[c] The reaction performed at reflux condition.
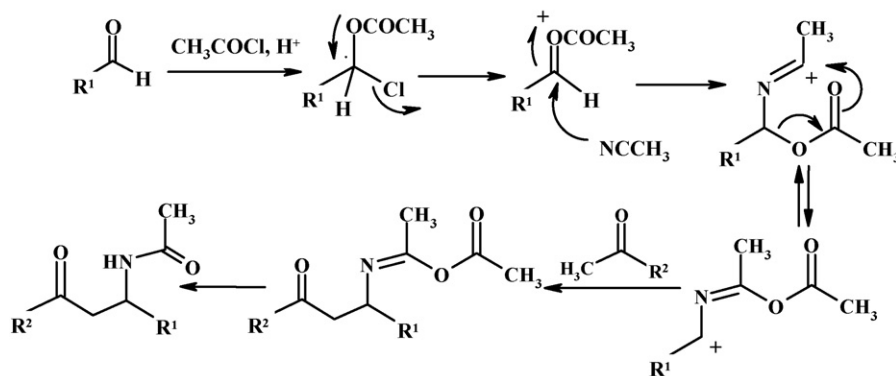
Scheme 2. Suggested mechanism for the synthesis of β-acetamido ketone.

reaction with acetonitrile it affords the corresponding α-acetoxy amides which will react with the enolate form of the ketone to afford the imidate ester and then will yield the amide.

4. Conclusion

Dakin–West reaction is the best known route for the synthesis of β-acetamido ketones as versatile intermediates for the synthesis of biologically or pharmacologically important compounds. Synthesis of these compounds was examined by using HPAs based on different supports. The catalysts were prepared using the impregnation–evaporation technique. 40 wt.% of PW/KSF and PW/γ-Al$_2$O$_3$ gave high activities compared to the other catalysts. The excellent yields were obtained within short reaction time by using PW/K 10. But the reusability of the catalyst was found to be unfavorable. When SiO$_2$ and carbon was used as supports, high yields were reached later than when the other supports were used.

In summary, supported HPAs were found to be highly efficient, reusable, inexpensive and ecofriendly solid acid catalysts for the synthesis of β-acetamido ketones. High yields of the products, short reaction times, mild reaction conditions and simple experimental procedure and product isolation make this protocol complementary to the existing methods.

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