Short communication

Vanadium-Substituted Tungstophosphoric Acid ($H_5PV_2W_{10}O_{40}$): A Green and Reusable Catalyst for Highly Efficient Acetylation of Alcohols and Phenols under Solvent-free Conditions

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Abstract

Vanadium-substituted tungstophosphoric acid, $H_5PV_2W_{10}O_{40}$ (HPVW), was used as a novel, efficient and green catalyst for acetylation of alcohols and phenols under solvent-free conditions. Various primary, secondary and tertiary alcohols were acetylated with acetic anhydride as an acetylating agent under solvent-free conditions in the presence of catalytic amount of HPVW at room temperature. The corresponding acetates were obtained in excellent yields within a very short reaction time. The catalyst can be recycled several times, so that this process could find useful applications. Also, phenols were acetylated in quantitative yield albeit after longer reaction time in comparison with alcohols. The selective acetylation of an alcoholic OH group in the presence of a phenolic OH group could be achieved by the appropriate choice of the reaction time. The excellent activity of HPVW was demonstrated by the high yields obtained for acetylation of alcohols and phenols having electron-withdrawing substituents.

Keywords: Acetylation, alcohols, phenols, solvent-free conditions, heteropoly acid, $H_5PV_2W_{10}O_{40}$.

1. Introduction

The acetylation of alcohols and phenols is a fundamental process in organic chemistry. It also provides an efficient route for protecting OH groups during oxidation, peptide coupling and glycosidation reactions.[1,2] The OH group protection is commonly achieved through aceylation with acetic anhydride due to the ease of deprotection.[3] The various catalysts for aceylation were developed, including nucleophilic agents such as Bu_3P[4] and DMAP,[5] Lewis acids such as metal halides,[6–8] metal perchlorates,[9–12] metal triflates,[13–18] $ZrOCl_2·8H_2O$,[19] metal–salen complexes,[20] iodine,[21] manganese(III) acetylacetonato complexes,[22] $Sn(IV)(TPP)(BF_4)_2$,[23] and several solid acids such as metal oxides,[24,25] montmorillonites,[26,27] $HClO_4$–SiO_2,[28] $AlPW_{12}O_{40}$,[29] zeolites,[30] HBF_4–SiO_2,[31] silica embedded–triflate catalysts,[32] and sulphated zirconia.[33] Some of these catalytic systems are homogeneous, non-recoverable and suffer from the limitations like longer reaction times, stringent conditions, use of halogenated solvents and hazardous materials; e.g., DMAP is highly toxic,

Bu_3P is flammable and air sensitive, perchloric acid and its salts are potentially explosive, and triflates are not cost effective. Furthermore, many of these methods are applicable only for the acetylation of alcohols. Therefore, the development of new methods and catalysts for acetylation of alcohols and phenols is still demanded.

Keggin-type heteropoly acids (HPAs) catalyze the transformation of various kinds of functional groups because their redox and acid properties can be controlled at the atomic or molecular level through a change of the constituent elements.[34,35] It is well-known that the catalytic activity of HPAs can be improved when other transition metal ions substitute Mo(VI) or W(VI) ions in the octahedral MO_6 groups of the Keggin structure.[36]

In this context, the catalytic function of substituted HPAs has attracted much attention and Keggin-type vanadium-substituted HPAs such as $H_4PVMo_{11}O_{40}$, $H_5PV_2Mo_{10}O_{40}$, and $H_6PV_3Mo_9O_{40}$ have been reported to be catalytically more active than simple $H_3PMo_{12}O_{40}$.[37,38] High activity of vanadium-containing HPAs prompted us to explore these compounds as catalysts for the conversion of

alcohols and phenols to their corresponding esters. In this paper, we report on a simple, rapid and efficient method for the acetylation of alcohols and phenols with acetic anhydride under solvent-free conditions in the presence of a green and recyclable vanadium-substituted HPA, $H_5PV_2W_{10}O_{40}$, abbreviated herein as HPVW.

2. Results and Discussion

2. 1. Catalyst Characterization

First, the HPVW catalyst was prepared and characterized by TGA, elemental analysis, FT-IR and UV spectroscopy, and potentiometeric titration. The TGA showed that the total percent of weight loss is 6.41%, which confirms that each HPA molecule has 10 molecules of water. In the IR spectrum of HPVW the characteristic bands denoting HPA with Keggin structure were observed: 1088 $\nu(P–O)$; 998 $\nu(W–O_d)$; 890 $\nu(W–O_b–M, M=W$ and $V)$; 778 $\nu(W–O_c–M)$.[39] Also, two bands at around 3400 and 1650 cm^{-1} were assigned to the stretching vibration of O–H bonds and the bending vibration of H–O–H bonds of crystalline waters, respectively.

In the Keggin structure, intense absorption bands at about 200 and 260 nm are caused by charge-transfer of the terminal oxygen and bridge-oxygen to metal atoms, respectively. In the UV-Vis spectrum of the catalyst are two characteristic bands at 205 ($O_d{\rightarrow}W$ CT) and 260 nm ($O_{b/c}{\rightarrow}W$ CT), respectively.[40]

The hydrogen atom numbers in the HPA and the ionization state can be determined by potentiometric titration. In the potentiometric titration curve (Fig. 1), the [OH]/[HPA] is 5 at the end point, which shows that there are five protons in the HPA and the electric charge of the heteropoly anion is five. All five protons are equivalent and are dissociated in one step.
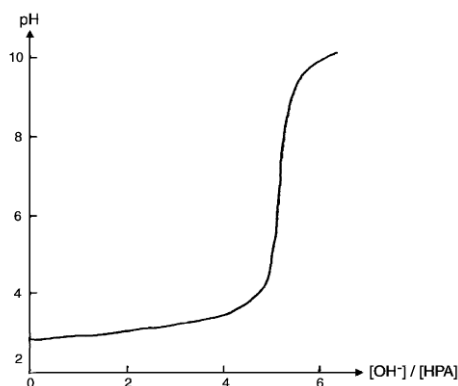

Fig. 1. The potentiometric titration curve of HPVW catalyst.

All data reported herein confirm that the accurate molecular formula of used HPA is $H_5PV_2W_{10}O_{40}10H_2O$ with Keggin structure.

2. 2. Catalytic Activity of HPVW for the Acetylation Reaction

The main objective of this work was to investigate the activity of HPVW as the heterogeneous catalyst for the acetylation reaction. Our investigation began with 1-phenylethanol (**1**) as a model substrate to test the catalytic activity of HPVW for acetylation of alcohols and to optimize the reaction conditions. In an initial experiment, when a heterogeneous mixture of alcohol (**1**, 1 equiv.), acetic anhydride (1.5 equiv.), and HPVW (~3 mol %) was stirred at room temperature under solvent-free conditions, the corresponding acetate (**2**) formed as the only product in 95% yield within 4 min in agreement with Scheme 1.
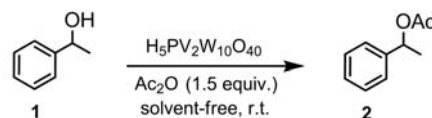
Scheme 1

The model reaction was also investigated in a variety of solvents including acetonitrile, toluene, dichloromethane, chloroform and THF at room temperature. As shown in Table 1, the best result in terms of reaction time and product yields has been achieved when the reaction is carried out without solvent. Therefore, the acetylation reactions were carried out thereafter under solvent-free conditions. It is interesting to mention that the acetylation of **1** with acetic anhydride did not proceed in the absence of catalyst.
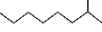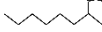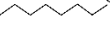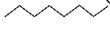
Table 1. Acylation of 1-phenylethanol with acetic anhydride in different solvents over HPVW. [a]

Entry	Solvent	Time (min)	Yield (%)[b]
1	CH_3CN	60	80
2	toluene	60	45
3	CH_2Cl_2	80	70
4	$CHCl_3$	65	60
5	THF	60	60
6	neat	4	95[c]

[a]Reaction conditions were the same as reported in general procedure in the Experimental part. [b]Yields determined with GC-MS. [c]Isolated yield.

To explore the potential of this catalytic system, we studied the acetylation of various alcohols under similar conditions. The results are summarized in Table 2. As one can see from Table, all alcohols were selectively converted to the corresponding acetates in quantitative yields without any evidence for the formation of side products. The general efficiency of this reaction is evident from the variety of hydroxy compounds, including primary, secon-

Table 2: Results of HPVW calalyzed acetylation of alcohols with acetic anhydride.[a]

Entry	Alcohol	Product[b]	Time (min)	Yield (%)[c]	Entry	Alcohol	Product[b]	Time (min)	Yield (%)[c]
1			5	95	28			5	94
2			4	95	29			3	90
3			4	96	30			10	86[d]
4			3	95	31			10	86[d]
5			5	95	32			12	88[d]
6			3	95	33			15	85
7			6	95					
8			5	92					
9			5	94					
10			4	90					
11			5	95					
12			5	95					
13			7	91					
14			4	92					
15			4	96					
16			4	95					
17			3	95					
18			4	93					
19			6	82					
20			3	94					
21			5	92					
22			3	92					
23			5	90					
24			4	92					
25			4	93					
26			3	94					
27			3	94					

[a]Reaction conditions were the same as reported in general procedure in the Experimental part. [b]All products were characterized on the basis of mass, IR and ^{1}H NMR data, and compared with authentic samples or reported data. [c]Isolated yied. [d]Yields determined with GC-MS.

dar and tertiary benzylic alcohols which reacts in excellent yields and in short reaction times.

The acetylation of a wide range of ring-substituted primary benzyl alcohols having various electron-donating and withdrawing groups was investigated with acetic anhydride over HPVW. These alcohols were efficiently converted to their corresponding acetates in excellent yields and the nature of substituents had no significant effect on the yields of products (Table 2, entries 1–14). Also, anthracene-9-methanol gave the corresponding acetate in high yield (Table 2, entry 15). With this method, various secondary alcohols were converted with high selectivity to their corresponding acetates (Table 2, entries 16–21). The behavior observed for the primary benzylic systems also seems to be prevalent in the case of secondary benzylic systems. That is, the presence of an electron-donating or an electron-withdrawing group on the aromatic ring did not have an appreciable effect on the reaction times and yields.

Furthermore, heterocyclic alcohols were converted to the corresponding acetates in very high yields (Table 2, entries 22–25). α,β-Unsaturated alcohol such as Cinnamyl alcohol was selectively converted to the corresponding acetate and carbon-carbon double bond remained intact under the reaction conditions (Table 2, entry 26). Aliphatic and non-benzylic alcohols were also converted into the corresponding acetates with high efficiency under the same reaction conditions (Table 2, entries 27–32). It is noteworthy that sterically hindered tertiary alcohol such as triphenylmethanol can also be acetylated with high yields albeit with longer reaction time (Table 2, entry 33). There was no elimination product in the mixture as shown by GC–MS analysis.

It seems that among the various hydroxy groups studied, the benzylic OH group was found to be most reactive. Further evidence that supports this statement can be drawn from the observation that acetylation of 1-phenyl-1,2-ethanediol (**3**) with 1 equivalent of acetic anhydride exclusively resulted in the acetylated product **4** (Scheme 2).
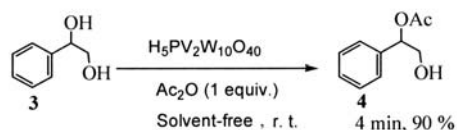
Scheme 2

The scope of this methodology was further extended for acetylation of phenols. As shown in Table 3, phenol and differently substituted phenols were acetylated in quantitative yields albeit after longer reaction times in comparison with alcohols. The excellent activity of HPVW was demonstrated by the high yields obtained for phenols having electron withdrawing groups (Table 3, entries 7 and 8).

Table 3: Results of HPVW calalyzed acetylation of phenols with acetic anhydride.[a]

Entry	Alcohol	Product[b]	Time (min)	Yield (%)[c]
1	⬡—OH	⬡—OAc	24	88
2	Me—⬡—OH	Me—⬡—OAc	16	95
3	Cl—⬡—OH	Cl—⬡—OAc	20	95
4	Me-⬡—OH	Me-⬡—OAc	16	94
5	Br—⬡—OH	Br—⬡—OAc	20	93
6	Cl,Cl—⬡—OH	Cl,Cl—⬡—OAc	25	92
7	O_2N—⬡—OH	O_2N—⬡—OAc	28	89
8	O_2N,NO_2—⬡—OH	O_2N,NO_2—⬡—OAc	35	85
9	naphthyl-OH	naphthyl-OAc	20	92
10	⬡—SH	⬡—SAc	25	86

[a]Reaction conditions were the same as reported in general procedure in the Experimental part. [b]All products were characterized on the basis of mass, IR and ^{1}H NMR data, and compared with authentic samples or reported data. [c]Isolated yield.

The acetylation of phenols needs longer reaction times, therefore the selective acetylation of an alcoholic OH group in the presence of a phenolic OH group could be achieved by the appropriate choice of the reaction time. For example, *p*-hydoxybenzyl alcohol gave only *p*-hydroxybenzyl acetate with 94% yield after a very short reaction time (5 min) at room temperature. Also, when a mixture of benzyl alcohol and phenol was stirred in the presence HPVW under solvent-free conditions, the former was converted to the corresponding acetate in 96% GC yield and the latter remained unchanged within 5 minutes.

HPVW could be easily recovered, by its simple filtration from the reaction mixture. The recovered catalyst was used for recycling, and deactivation of HPVW was hardly observed in acetylation of **1** even after four catalytic cycles (see Table 4). At the same time, the concentration of W and V in the filtrate was determined to be less than 1% by ICP-AES analysis. On the other hand, the IR and UV-VIS spectra of the recovered catalyst were identical with fresh catalyst. All these findings confirm that leaching of catalyst did not take place under the conditions investigated.

Table 4 The recyclability of the catalyst in the acetylation of 1-phenylethanol (Scheme 1).[a]

Cycle	0	1st	2nd	3rd	4th
Yield of **2** (%)	95	93	94	91	92

[a]Reaction conditions were the same as reported in general procedure in the Experimental part.

The experiments, usually performed on a 2 mmol scale, can be scaled up to 100 mmol without difficulties. A reaction of 100 mmol of 1-phenylethanol under the present conditions gave the corresponding acetate in 94% isolated yield.

To find out the efficiency of HPVW as a general esterification catalyst, 1-phenylethanol (**1**) was treated with various anhydrides under same reaction conditions (Table 5). In comparison with acetic anhydride, the reactions with higher anhydrides took longer times at room temperature. However, the reactions were completed in 13–25 minutes under solvent-free conditions affording the corresponding esters in excellent yields (88–92%). It seem that the rate of esterification was influenced by the steric and electronic factors of anhydrides and followed the order Ac_2O > $(EtCO)_2O$ > $(i–PrCO)_2O$ > $(tert–BuCO)_2O$ > $(PhCO)_2O$. The longer times (13–15 min) required for the reaction with $(EtCO)_2O$, $(i–PrCO)_2O$ and $(t–BuCO)_2O$ were mainly due to the steric effect of the alkyl groups of these anhydrides (compare entry 1 with entries 2–4 in Table 5). The longer reaction time and the requirement of 2 equivalents of $(PhCO)_2O$, as compared to 1.5 equiv. of Ac_2O (compare entries 1 and 5, Table 5), were due to the combined effect of the steric and electronic factors of the phenyl group in $(PhCO)_2CO$. The phenyl group makes the carbonyl group in $(PhCO)_2O$ less electrophilic due to the resonance effect.

| Entry	Anhydride	Time (min)	Yield (%)[b]
1	Ac_2O	4	95
2	$(EtCO)_2O$	13	92
3	$(^iPrCO)_2O$	15	91
4	$(^tBuCO)_2O$	18	90
5	$(PhCO)_2O^c$	25	88

[a]Reaction conditions were the same as reported in general
procedure in the Experimental part.
[b]Isolated yields of the corresponding acylated product.
[c]2 equivalents of $(PhCO)_2O$ was used.

The activity of sodium salt of catalyst, $Na_5PV_2W_{10}O_{40}$, was also tested for the model reaction (see Scheme 1). Under this condition, the yield of acetylated product (**2**) was only 28% after 1 hour. This test confirms that the catalytic activity of HPVW arises mainly from its very strong Brönsted acidity. Solid HPAs possess a discrete ionic structure, comprising fairly mobile basic structural units – polyanions and countercations (H^{+}, H_3O^+, $H_5O_2^+$, etc.) – unlike the network structure of zeolites and metal oxides.[34] This unique structure manifests itself to exhibit an extremely high catalytic activity in acid-catalyzed acetylation of alcohols under solvent-free conditions.

Table 6 lists the results for the acetylation of benzyl alcohol with acetic anhydride in the presence of various catalysts under our reaction conditions. Among the HPAs tested, vanadium-substituted HPAs were the most effective catalysts, and the yield decreased in the order $H_6PV_3Mo_9O_{40}$ > $H_5PV_2W_{10}O_{40}$ ≈ $H_5PV_2Mo_{10}O_{40}$ > $H_4PVW_{11}O_{40}$ >> $H_3PW_{12}O_{40}$ ≈ $H_3PMo_{12}O_{40}$. The vanadium-substituted HPAs exhibited higher catalytic activity than those of $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$, showing that vanadium is an indispensable component for attaining high yields in the acetylation reactions.

Table 6: Acetylation of benzyl alcohol in the presence of various HPAs.[a]
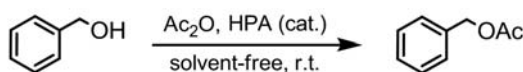
Entry	HPA	Time (min)	Yield[b] (%)
1	$H_6PV_3Mo_9O_{40}$	2	95
2	$H_5PV_2W_{10}O_{40}$	5	95
3	$H_5PV_2Mo_{10}O_{40}$	4	95
4	$H_4PVW_{11}O_{40}$	12	90
5	$H_3PW_{12}O_{40}$	60	75
6	$H_3PMo_{12}O_{40}$	60	70

[a]Reaction conditions were the same as reported in general procedure in the Experimental part. [b]Isolated yield.

Although it is difficult to offer an explanation for the different activity between these HPAs, certainly there is a complex relationship between the activity and structure of polyanion. By changing the constituent elements of polyanion, the acid strength of HPA as well as its catalytic activity is able to vary in a wide range.[35] Also; transition metal ions have an important effect on the catalytic properties of these compounds when they substitute tungsten (VI) ions in the octahedral WO_6 groups of the Keggin structure.

On the basis of the above observations and reported mechanisms,[38,41] the following catalytic cycle is proposed for the acetylation of alcohols and phenols in the presence of HPVW (Scheme 3). According to this suggestion, the carbonyl group of acetic anhydride is activated by coordinating of proton from the solid HPVW. Reaction of alcohol with the activated C=O resulted in the corresponding acetate and acetic acid.
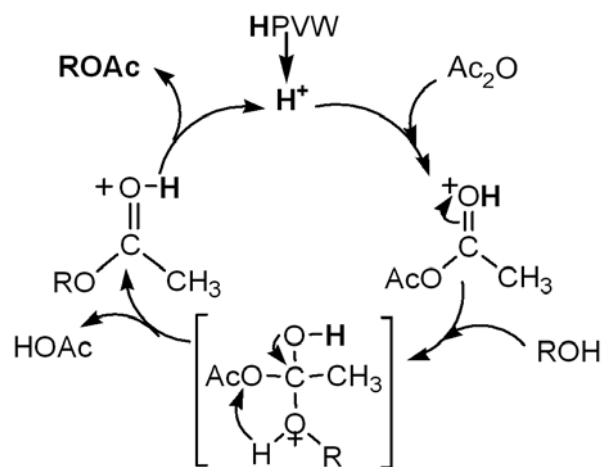
Scheme 3: The proposed catalytic cycle for acetylation of alcohols and phenols.

As shown in Table 6, the mono, di, and trivanadium substituted HPAs are highly active in acetylation reaction in comparison with parent $H_3PW_{12}O_{40}$, suggesting that the V–O–W and V=O centers are the active sites in catalyst which participate in the activation of carbonyl group of acetic anhydride. In fact, it seems that HPVW acts not only as the Brönsted acid but also as the Lewis acid, and accelerates the acetylation reaction.

3. Conclusions

In conclusion, we have presented a mild, efficient and green acetylation method for various alcohols and phenols using acetic anhydride as an acetylating agent in the presence of catalytic amount of HPVW without sol-

vent. Benzylic and non-benzylic hydroxy groups can be efficiently converted into corresponding acetates within very short reaction times. It is noteworthy that the catalyst can be used for subsequent acetylation cycles without observable loss of its catalytic activity. In contrast to many other acids, storage of this non-hygroscopic and non-corrosive solid heteropoly acid does not need special precautions, e.g., it can be stored on a bench top for months without losing its catalytic activity.

4. Experimental

All chemicals and solvents were purchased from Merck Company and used as received. The HPVW catalyst was prepared according to modified published procedure.[42] and characterized by TGA, elemental analysis, FT-IR and UV-Vis spectroscopy, and potentiometric titration as follows The amount of tungsten, vanadium and phosphor in catalyst were analyzed by ICP spectrometer and its water content was determined by thermogravimetry. Infrared spectrum was recorded on Shimadzu FT-IR 8400 spectrophotometer.

4. 1. Preparation of Catalyst

Sodium metavanadate ($NaVO_3$, 12.2 g, 100 mmol) was dissolved in 50 mL of boiling water and mixed with disodium hydrogen phosphate (Na_2HPO_4, 3.55 g, 25 mmol), dissolved in 50 mL of water. After cooling the resulting solution to room temperature, concentrated sulfuric acid (5 mL, 17 M, 85 mmol) was added to give a red solution. Sodium tungstate dihydrate ($Na_2WO_4.2H_2O$, 82.5 g, 250 mmol) was dissolved in 100 mL of water and added to the red solution with vigorous stirring, followed by slow addition of concentrated sulfuric acid (42 mL, 17 M, 714 mmol). Extraction of the solution with diethyl ether (500 mL), followed by evaporation in air, afforded the HPVW product as a crystalline, orange-red solid (yield, 74%). TG analysis indicated 10 water molecules per HPA. Elemental analysis calculated for $H_5PV_2W_{10}O_{40}.10H_2O$: P, 1.10 ; V, 3.64; W, 65.74; H_2O, 6.44. Found: P, 1.13 ; V, 3.71; W, 64.68;H_2O, 6.41. FT–IR (KBr), ν (cm^{-1}): 3400 (O–H), 1650 (O–H), 1088 (P–O), 998 (W–O_d), 890 (W–O_b–M, M=W and V), and 778 (W–O_c–M) (O_a, inner oxygen; O_b, corner-shared oxygen; O_c, edge-shared oxygen; O_d, terminal oxygen). UV–Vis spectrum (CH_3CN, λ_{max}, nm): 205 (O_d→M CT); 260 ($O_{b/c}$→M CT).

4. 2. General Procedure for Acetylation of Alcohols and Phenols

To a mixture of alcohol or phenol (2 mmol) and acetic anhydride (3 mmol), was added HPVW (100 mg). The mixture was stirred at room temperature for a specified time. The progress of the reaction was monitored by TLC and/or GC-MS. After completion of the reaction, CH_2Cl_2 (2 × 15 mL) was added and the catalyst was filtered. The filtrate was washed with 10% $NaHCO_3$ (15 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford the product. The results are shown in Tables 2 and 3. All products are known and were identified by comparison of their physical and spectroscopic data (m.p., TLC, IR, ^{1}HNMR and MS) with those of authentic samples or literature data.

4. 3. Catalyst Recovery and Reuse

The recovery and reusability of the catalyst was investigated in the acetylation of 1-phenylethanol (**1**). After completion of the reaction, CH_2Cl_2 was added and the catalyst was separated. The recovered catalyst was dried at 60 °C for 1 h and used in the next run. Four consecutive runs were checked. The results are summarized in Table 4. The results showed that the catalyst can be reused without significant loss of its activity.

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Povzetek

Z vanadijem substituirana volfram-fosforjeva kislina, $H_5PV_2W_{10}O_2$ (HPVW), je bila uporabljena kot nov, učinkovit in zelen katalizator za acetiliranje alkoholov in fenolov, brez uporabe topil. Na ta način so bili acetilirani različni primarni, sekundarni in terciarni alkoholi z uporabo acetanhidrida kot acetilirnega sredstva, v prisotnosti katalitskih količin HPVW in brez dodatne uporabe topil, pri sobni temperaturi. Ustrezni acetati kot produkti so nastali z odličnimi izkoristki v zelo kratkem reakcijskem času. Katalizator po reakciji lahko večkrat recikliramo, zato ima ta reakcija tudi uporabno vrednost. Po enakem postopku lahko kvantitativno acetiliramo tudi fenole, za pretvorbo pa potrebujemo daljše reakcijske čase. Z ustrezno izbiro reakcijskega časa lahko selektivno acetiliramo alkoholno OH skupino v prisotnosti fenolne OH skupine. Odlična aktivnost HPVW kot katalizatorja se je še posebej pokazala pri acetiliranju alkoholov in fenolov, ki vsebujejo elektron-privlačne skupine.