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Decatungstodivanadogermanic heteropoly acid ($H_6GeW_{10}V_2O_{40}.22H_2O$): A novel, green and reusable catalyst for efficient acetylation of alcohols and phenols under solvent-free conditions

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ABSTRACT

Decatungstodivanadogermanic acid ($H_6GeW_{10}V_2O_{40}.22H_2O$) was used as a novel and green heterogeneous catalyst for the acetylation of hydroxy compounds under solvent-free conditions at room temperature. Efficient and selective acetylation of various alcohols and phenols was conducted with acetic anhydride as an acetylating agent over $H_6GeW_{10}V_2O_{40}.22H_2O$ under solvent-free conditions. All acetylated products were selectively obtained in excellent yields with very short reaction times. The reaction times were longer for the acetylation of phenols than for alcohols, so that an alcoholic OH group could be selectively acetylated in the presence of a phenolic OH group by the appropriate choice of reaction time. The catalyst can be recycled several times without observable loss of activity and selectivity.

1. Introduction

The protection of hydroxyl groups of alcohols and phenols is an important and widely used transformation in organic synthesis [1]. Among the various protection methods, acetylation was found to be the most common method which is typically performed using acetic anhydride in the presence of basic or acidic catalysts [1,2]. Numerous catalytic methods have been reported for this transformation [3-21] but most of them are homogeneous and non-recoverable. In addition, they have one or more disadvantages such as prolonged reaction times, low yields, harsh conditions, use of harmful organic solvents, tedious work-up procedures, use of excess reagent/catalyst, use of explosive, moisture-sensitive and/or expensive catalysts.

The use of heterogeneous catalysts is one of the most promising solutions to reduce the above mentioned problems. Heterogeneous catalysts offer several advantages over homogeneous systems with respect to easy recovery and recycling of catalysts as well as the minimization of undesired toxic wastes. In this framework, several metal oxides and supported systems including YO_2–ZrO_2 [22], ZnO [23], transition metal oxides [24], montmorillonites [25], $HClO_4$-SiO_2 [26], H_2SO_4-SiO_2 [27], $AlPW_{12}O_{40}$ [28], zeolites [29], Nafion-H [30], HBF_4-SiO_2 [31], KF-Al_2O_3 [32], MoO_3-Al_2O_3 [33], $NaHSO_4$-SiO_2 [34], sulphated zirconia [35] and $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$ [36] [TMBSA][HSO_4] ionic liquid [37], silica-bonded cobalt(II) salen [38], and silica-bonded *N*-propyl sulfamic acid and *S*-propyl sulfuric acid [39,40] have been used as heterogeneous catalysts for the acetylation of alcohols and phenols. However, each of these methods has advantages and limitations.

Heterogeneous acid catalysis by heteropoly acids (HPAs) has attracted much interest because of its potential of great economic rewards and green benefits [41-43]. Unlike metal oxides and zeolites, HPAs possess very strong Brönsted acidity and their acid sites are more uniform and easier to control than those in other solid acid catalysts. These properties make them suitable solid heterogeneous catalysts for organic transformations. In continuation of our interest in exploring green heterogeneous catalysts for organic transformations [44-46], in the present work we report on the use of $H_6GeW_{10}V_2O_{40}.22H_2O$ as a new andgreen recyclable hetero geneous catalyst for the efficient acetylation of alcohols and phenols with acetic anhydride under solvent-free conditions. To the best of our knowledge, this is the first report regarding the use of a Ge and V-substituted HPA for the acetylation reaction.

2. Experimental

All alcohols and phenols were commercially available and used without further purification. The solvents were spectroscopic grade. $H_6GeW_{10}V_2O_{40}.22H_2O$ was prepared according to the method reported [47,48]. All products were identified through the comparison of their physical and spectral data (M.p., TLC, FT-IR, GC-MS and ^{1}H-NMR) with those of authentic samples or reported data. Infrared spectra were recorded on a Shimadzu system FT–IR 160 instrument.

2.1. Instrumentation

^{1}H-NMR spectra were recorded on a Bruker 500 MHz spectrometer in $CDCl_3$ with $SiMe_4$ (TMS) as internal reference. GC-MS analysis was carried out on a Shimadzu QP 5050 GC-MS

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instrument. Melting points were measured by an Electrothermal-9200 melting point apparatus.

2.2. Synthesis of catalyst

$H_6GeW_{10}V_2O_{40}\cdot 22H_2O$ was prepared according to the literature as follows [47,48]. 0.8 g of GeO_2 was dissolved in a hot solution of 10% NaOH and a solution of 22.8 g of $Na_2WO_4\cdot 2H_2O$ in 100 mL of hot water was added to get mixture A. The pH of A was adjusted to 6 with HCl (1:1) and heated for 1 h. Then a solution of 7.5 g of Na_2CO_3 dissolved in 25 mL of hot water was added. The mixture was concentrated to 100 mL by heating. 2.4 g of $NaVO_3\cdot 2H_2O$ and 2.5 g of $Na_2WO_4\cdot 2H_2O$ were dissolved in 30 mL of hot water, respectively, and the two solutions were mixed to get mixture B. The pH of B was adjusted to 2.5 with H_2SO_4 (1:1). Then A was added dropwise, and the pH was kept 2.5 while dropping. After stirring for 3 h at 60 °C, the solution was cooled to room temperature. The cooled solution was extracted with ether in sulfuric acid medium and the extractant was dissolved with a small amount of water. After the ether was evaporated, the remaining solution was placed in the desiccator until orange crystals were separated out. The final yield was about 70%. Anal. Calcd. for $H_6GeW_{10}V_2O_{40}.22H_2O$: Ge, 2.38; W, 60.18; V, 3.33, H_2O, 12.97. Found: Ge, 2.38; W, 60.06; V, 3.29; H_2O, 12.95 % (TG analysis). FT-IR (KBr, cm^{-1}): 3450 ν(O-H); 1620 δ(O-H); 964 ν_{as}(M–O_d); 885, ν_{as}(M–O_b–M); 818 ν_{as}(Ge–O_a); 780 ν_{as}(M–O_c–M); 464 δ(O–Ge–O), (M=W and V; O_a, inner oxygen; O_b, corner-shared oxygen; O_c, edge-shared oxygen; O_d, terminal oxygen) [47,48]. UV-Vis spectrum (CH_3CN, λ_{max}, nm): 205 ($O_d\rightarrow$M, CT); 262 ($O_{b/c}\rightarrow$M, CT).

2.3. General procedure for the acetylation of alcohols and phenols catalyzed by $H_6GeW_{10}V_2O_{40}.22H_2O$

To a mixture of alcohol or phenol (5 mmol) and acetic anhydride (5 mmol), was added $H_6GeW_{10}V_2O_{40}.22H_2O$ catalyst (1.32 mol %). The mixture was stirred at room temperature for the time indicated in Tables 1 and 2. The progress of the reaction was followed by TLC and/or GC-MS. After completion of the reaction, ethyl acetate (2×10 mL) was added, and the catalyst was filtered. The filtrate was washed with 15 mL of a 10 % aqueous solution of $NaHCO_3$ and dried with Na_2SO_4. The solvent was removed under reduced pressure to afford the product. The results are shown in Tables 1 and 2. All products are known and were identified by comparing their physical and spectral data (M.p., TLC, IR, ^{1}H-NMR and GC-MS) with those of the authentic samples or literature data.

2.4. Catalyst recovery

The reusability of the catalyst was investigated in the acetylation of benzyl alcohol. After completion of the reaction, ethyl acetate was added and the catalyst was separated. The recovered catalyst was dried and reused in the next run. Five consecutive runs were checked. The results are summarized in Table 3.

^{1}H NMR data for the some of the acetylated products:

Benzyl acetate (Table 2, entry 1): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.35 (m, 5H, Ar*H*), 5.08 (s, 2H, CH_2), 2.06 (s, 3H, O*Ac*).

4-Methoxybenzyl acetate (Table 2, entry 3): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.28 (d, *J* = 8.5 Hz, 2H, Ar*H*), 6.88 (d, *J* = 8.5 Hz, 2H, Ar*H*), 5.02 (s, 2H, CH_2), 3.78 (s, 3H, OCH_3), 2.05 (s, 3H, O*Ac*).

3-Methoxybenzyl acetate (Table 2, entry 4): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.22 (t, *J* = 8.5 Hz, 1H, Ar*H*), 6.9-6.8 (m, 3H, Ar*H*), 5.03 (s, 2H, CH_2), 3.75 (s, 3H, OCH_3), 2.05 (s, 3H, O*Ac*).

4-Bromobenzyl acetate (Table 2, entry 5): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.33 (d, *J* = 8.95 Hz, 2H, Ar*H*), 7.28 (d, *J* = 8.95 Hz, 2H, Ar*H*), 5.07 (s, 2H, CH_2), 2.1 (s, 3H, O*Ac*).

2,4-Dichlorobenzyl acetate (Table 2, entry 6): M.p.: 61-63 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.66 (d, *J* = 2.3 Hz, 1H, Ar*H*); 7.37 (dd, *J* = 8.8, 2.3 Hz, 1H, Ar*H*), 6.77 (d, *J* = 8.8 Hz, 1H, Ar*H*), 5.22 (s, 2H, CH_2), 2.15 (s, 3H, O*Ac*).

2-Chlorobenzyl acetate (Table 2, entry 7): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.38-7.32 (m, 2H, Ar*H*), 7.28-7.2 (m, 2H, Ar*H*), 5.21 (s, 2H, CH_2), 2.10 (s, 3H, O*Ac*).

4-Nitrobenzyl acetate (Table 2, entry 8): M.p.: 76-78 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.25 (d, *J* = 9.3 Hz, 2H, Ar*H*), 7.53 (d, *J* = 9.3 Hz, 2H, Ar*H*), 5.22 (s, 2H, CH_2), 2.15 (s, 3H, O*Ac*).

4-Triflouromethylbenzyl acetate (Table 2, entry 11): M.p.: 58-60 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.12 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.43 (d, *J* = 8.8 Hz, 2H, Ar*H*), 5.32 (s, 2H, CH_2), 2.18 (s, 3H, O*Ac*).

4-Cyanoobenzyl acetate (Table 2, entry 12): M.p.: 66-67 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.17–8.22 (m, 2H, Ar*H*), 7.45–7.48 (m, 2H, Ar*H*), 4.78 (s, 2H, CH_2), 2.15 (s, 3H, O*Ac*).

3-acetylbenzyl acetate (Table 2, entry 14): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.86 (s, 1H, Ar*H*), 7.26 (m, 3H, Ar*H*), 2.58 (s, 3H), 2.11 (s, 3H, O*Ac*).

1-Acetoxy-1-phenyl ethane (Table 2, entry 14): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.41-7.30 (m, 5H, Ar*H*), 5.92 (q, *J* = 6.65 Hz, 1H, OC*H*-), 2.07 (s, 3H, O*Ac*), 1.54 (d, *J* = 6.56 Hz, 3H, CH_3).

1-Acetoxy-1-phenyl propane (Table 2, entry 16): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.33 (s, 5H, Ar*H*), 5.68 (t, *J*= 7.4 Hz, 1H, CH), 2.06 (s, 3H, O*Ac*), 1.9 (m, 2H, CH_2), 0.92 (t, *J* = 8.1 Hz, 3H, CH_3).

Diphenylmethyl acetate (Table 2, entry 17): M.p.: 39-41 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.38-7.27 (m, 10H, Ar*H*), 7.00 (s, 1H, C*H*), 2.02 (s, 3H, O*Ac*).

2-Acetoxy-2-phenyl acetophenone (Table 2, entry 18): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.95 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.56-7.50 (m, 3H, Ar*H*), 7.38-7.35 (m, 5H, Ar*H*), 6.90 (s, 1H, C*H*), 2.22 (s, 3H, O*Ac*).

Cinnamyl acetate (Table 2, entry 19): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.38-7.18 (m, 5H, Ar*H*), 6.66 (d, *J* = 15.6 Hz, 1H, C*H*), 6.27 (dt, *J* = 15.8 and 7.8 Hz, 1H, C*H*), 4.72 (d, *J* = 7.8 Hz, 2H, CH_2), 2.07 (s, 3H, O*Ac*).

1-Acetoxy-2-phenylethane (Table 2, entry 20): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.30-7.18 (m, 5H, Ar*H*), 4.26 (t, *J*=8.6 Hz, 2H, CH_2), 2.92 (t, *J* = 8.6 Hz, 2H, CH_2), 2.03 (s, 3H, O*Ac*).

1-Acetoxy-2-phenylpropane (Table 2, entry 21): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.40-7.26 (m, 5H, Ar*H*), 4.30-4.20 (d, 2H, CH_2), 3.15 (sextet, 1H, C*H*), 2.05 (s, 3H, O*Ac*), 1.32 (d, 3H, CH_3).

1-Acetoxy-3-phenylpropane (Table 2, entry 22): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.10-7.34 (m, 5H, Ar*H*), 4.10 (t, *J*=6.6 Hz, 2H, CH_2), 2.69 (t, *J* = 7.4 Hz, 2H, -CH_2-), 2.05 (s, 3H, O*Ac*), 1.90-2.01 (m, 2H, CH_2).

1-Methylheptyl acetate (Table 2, entry 23): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.85 (m, 1H, -OC*H*-), 2.03 (s, 3H, O*Ac*), 1.60–1.20 (m, 10H, 5CH_2-), 1.10 (d, *J*=6.5 Hz, 3H, -CH_3), 0.9 (t, *J*=6.6 Hz, 3H, -CH_2CH_3).

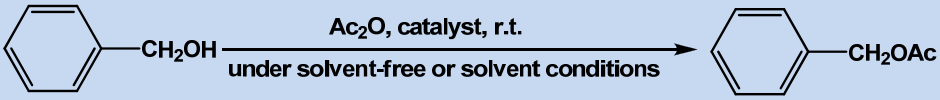
1-Heptyl acetate: (Table 2, entry 24): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.85–4.25 (t, *J*=6.8 Hz, 2H, CH_2), 2.02 (s, 3H, O*Ac*), 1.75–1.35 (m, 10H), 0.95 (t, *J*= 6.7 Hz, 3H,).

Cyclohexyl acetate (Table 2, entry 25): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.76-4.71 (m, 1H, C*H*), 2.04 (s, 3H, O*Ac*), 1.87-1.34 (m, 10H, CH_2).

1-Phenyl-1, 2-ethane-diol diacetate (Table 2, entry 27): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.36-7.26 (m, 5H, Ar*H*), 6.02 (dd, 1H, 7.6, 3.9 Hz, C*H*), 4.26-4.36 (m, 2H, CH_2), 2.11 (s, 3H, O*Ac*), 2.05 (s, 3H, O*Ac*).

Ethane-1,2-diol diacetate (Table 2, entry 28): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.21 (s, 4H, 2 CH_2).2.03 (s, 6H, 2O*Ac*).

Table 1. The reaction of benzyl alcohol with acetic anhydride under different conditions [a].



Entry	Catalyst	Amount (mol %)	Solvent (10 mL)	Time (min)	Yield (%)[b]
1	$H_6GeW_{10}V_2O_{40}.22H_2O$	0.33	—	35	38
2	$H_6GeW_{10}V_2O_{40}.22H_2O$	0.66	—	20	56
3	$H_6GeW_{10}V_2O_{40}.22H_2O$	0.99	—	15	82
4	$H_6GeW_{10}V_2O_{40}.22H_2O$	1.32	—	8	92
5	$H_6GeW_{10}V_2O_{40}.22H_2O$	1.65	—	8	93
6	$H_6GeW_{10}V_2O_{40}.22H_2O$	1.98	—	8	93
7	$H_6GeW_{10}V_2O_{40}.22H_2O$	0.00	—	30	Trace
8	$H_6GeW_{10}V_2O_{40}.22H_2O$	1.32	Acetonitrile	60	75
9	$H_6GeW_{10}V_2O_{40}.22H_2O$	1.32	Toluene	60	56
10	$H_6GeW_{10}V_2O_{40}.22H_2O$	1.32	Dichloromethane	80	70
11	$H_6GeW_{10}V_2O_{40}.22H_2O$	1.32	Chloroform	80	64
12	$H_3PMo_{12}O_{40}.nH_2O$	1.32	—	60	76
13	$H_3PW_{12}O_{40}.nH_2O$	1.32	—	60	79
14	$H_4SiW_{12}O_{40}.nH_2O$	1.32	—	60	72
15	$H_3PMo_{11}WO_{40}.nH_2O$	1.32	—	60	75
16	$(NH_4)_{2.5}HPW_{12}O_{40}.nH_2O$	1.32	—	60	93
17	GeO_2	1.32	—	60	Trace
18	$NaVO_3.2H_2O$	1.32	—	60	Trace
19	$NaWO_4.2H_2O$	1.32	—	60	Trace
20	$Ag_6GeW_{10}V_2O_{40}$	1.32	—	60	10

[a] Reaction conditions: benzyl alcohol (5 mmol), Ac_2O (5 mmol), in the presence catalyst (mol %), without or with solvent (10 mL) at r.t.
[b] Isolated yields.

Menthyl acetate (Table 2, entry 29): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.67 (dt, J=10.8 and 4.5 Hz, 1H, OC*H*-). 2.09 (s, 3H, -O*Ac*), 1.00-1.90 (m, 9H, 3-CH-, 3-CH_2-), 0.90 (d, J=7.2 Hz, 6H, 2CH_3), 0.78 (d, J=6.9 Hz, 3H, 2CH_3).

Phenyl acetate (Table 2, entry 30): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.40 (t, 2H, Ar*H*), 7.27 (t, 1H, Ar*H*), 7.12 (d, J = 7.36 Hz, 2H, Ar*H*), 2.32 (s, 3H, O*Ac*).

4-Methylphenyl acetate (Table 2, entry 31): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.18 (d J = 7.9 Hz, 2H, Ar*H*), 6.97 (d, J = 7.9 Hz, 2H, Ar*H*), 2.35 (s, 3H, CH_3), 2.27 (s, 3H, O*Ac*).

4-chlorophenyl acetate (Table 2, entry 33): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.50 (d, J = 8.4 Hz, 2H, Ar*H*), 7.00 (d, J = 8.4 Hz, 2H, Ar*H*), 2.31 (s, 3H, O*Ac*).

4-Nitrophenyl acetate (Table 2, entry 34): M.p.: 78-79 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.28 (d, J = 8.9 Hz, 2H, Ar*H*) 7.3 (d, J = 8.9 Hz, 2H, Ar*H*), 2.35 (s, 3H, O*Ac*).

1-Naphthyl acetate (Table 2, entry 36): M.p.: 43-45 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.89-7.83 (m, 2H, Ar*H*), 7.73 (d, J = 8 Hz, 1H, Ar*H*), 7.53-7.42 (m, 3H, Ar*H*), 7.24 (d, J = 7.5 Hz, 2H, Ar*H*), 2.45 (s, 3H, O*Ac*).

S-Phenyl thioacetate (Table 2, entry 37): Colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.41 (s, 5H, Ar*H*), 2.41 (s, 3H, O*Ac*).

1, 4-Diacetoxybenzene (Table 2, entry 38): M.p.: 68-69 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.1 (s, 4H, Ar*H*), 2.28 (s, 6H, O*Ac*).

3. Results and discussion

The aim of this work was to examine the activity of a vanadium-containing HPA, $H_6GeW_{10}V_2O_{40}.22H_2O$, as a novel heterogeneous catalyst for the acetylation of alcohols and phenols. Initial experiments were focused on the acetylation of benzyl alcohol as a model substrate to check the activity of this HPA and to optimize the reaction conditions (Table 1). In a typical reaction, a mixture of benzyl alcohol (5 mmol) and acetic anhydride (5 mmol) was stirred in the presence of catalyst under solvent-free conditions at room temperature. The progress of the reaction was monitored by TLC. To optimize the catalyst requirement, the catalyst amount was varied from 0.33 to 1.98 mol % per 5 mmol of benzyl alcohol. As shown in Table 1, the yield of benzyl acetate was increased with increase in the amount of catalyst, which is related to the proportional increase in the number of active sites. However, amounts greater than 1.32 mol% of catalyst produced no significant increase in the yield of product and hence all further experiments were carried out at this catalyst loading (Table 1; entries 1-6). The essential role played by the catalyst is evident from the extremely low yield of benzyl acetate found in the absence of it (Table 1; entry 7). The model reaction was also studied in several organic solvents including acetonitrile, toluene, dichloromethane and chloroform at room temperature. As shown in Table 2, the best result in terms of reaction time and product yield was achieved when the reaction was carried out without solvent. Therefore, all further reactions were investigated under solvent-free conditions.

The efficiency of $H_6GeW_{10}V_2O_{40}.22H_2O$ catalyst was compared with some common HPAs including $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{11}WO_{40}$, and $(NH_4)_{2.5}HPW_{12}O_{40}$ under the same reaction conditions. The results showed that in terms of reaction time and product yield, $H_6GeW_{10}V_2O_{40}.22H_2O$ catalyst is superior (Table 1, entries 12-16). 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 HPAs. By changing the constituent elements of HPAs (both hetero and addenda atoms), their acid strength and catalytic activity could be changed in a wide range [41]. Also, the transition metal cations such as V^{5+} have an important effect on the catalytic properties of these compounds when they substitute tungsten cations in the octahedral WO_6 groups of the Keggin structure [41].

We tested the effect of GeO_2, $NaVO_3.H_2O$, and $Na_2WO_4.2H_2O$ as the catalyst for the model reaction. As can be seen in Table 1, these compounds were not effective for the reaction (Table1, entries 17-19). The activity of the silver salt of the catalyst, $Ag_6GeW_{10}V_2O_{40}$, was also tested for the model reaction. Under this condition, the yield of benzyl acetate was about 10% after a long reaction time of 1 h (Table 1, entry 20). This test confirmed that the catalytic activity of the HPA arises mainly from its very strong Brönsted acidity.

To evaluate the generality and scope of this procedure, the acetylation of various alcohols was investigated under optimized conditions. The results are summarized in Table 2 which shows that all alcohols were selectively converted to the corresponding acetates with quantitative yields without any evidence of the formation of side products.

Table 2. Results of the acetylation of alcohols and phenols with acetic anhydride catalyzed by $H_6GeW_{10}V_2O_{40}.22H_2O$ [a].

Entry	Substrate	Product[b]	Time (min)	Yield (%)[c]
1	$C_6H_5CH_2OH$	$C_6H_5CH_2OAc$	8	92
2	4-pr^i-$C_6H_4CH_2OH$	4-pr^i-$C_6H_4CH_2OAc$	6	95
3	4-MeO-$C_6H_4CH_2OH$	4-MeO-$C_6H_4CH_2OAc$	6	94
4	3-MeO-$C_6H_4CH_2OH$	3-MeO-$C_6H_4CH_2OAc$	8	90
5	4-Br-$C_6H_4CH_2OH$	4-Br$C_6H_4CH_2OAc$	7	91
6	2,4-$(Cl)_2$-$C_6H_3CH_2OH$	2,4-$(Cl)_2C_6H_3CH_2OAc$	12	88
7	2-Cl-$C_6H_4CH_2OH$	2-Cl-$C_6H_4CH_2OAc$	10	90
8	4-NO_2-$C_6H_4CH_2OH$	4-NO_2-$C_6H_4CH_2OAc$	12	92
9	2-NO_2-$C_6H_4CH_2OH$	2-NO_2-$C_6H_4CH_2OAc$	14	88
10	3-NO_2-$C_6H_4CH_2OH$	3-NO_2-$C_6H_4CH_2OAc$	14	86
11	4-CF_3-$C_6H_4CH_2OH$	4-CF_3-$C_6H_4CH_2OAc$	15	85
12	4-CN-$C_6H_4CH_2OH$	4-CN-$C_6H_4CH_2OAc$	14	87
13	3-CHO-$C_6H_4CH_2OH$	3-CHO-$C_6H_4CH_2OAc$	13	84
14	3-MeCO-$C_6H_4CH_2OH$	3-MeCO-$C_6H_4CH_2OAc$	12	83
15	$C_6H_5CHOHCH_3$	$C_6H_5CH(OAc)CH_3$	8	95
16	$C_6H_5CHOHCH_2CH_3$	$C_6H_5CH(OAc)CH_2CH_3$	8	92
17	$(C_6H_5)_2CHOH$	$(C_6H_5)_2CHOAc$	10	93
18	$C_6H_5C(=O)CHOHC_6H_5$	$C_6H_5C(=O)CH(OAc)C_6H_5$	15	89
19	$C_6H_5CH=CHCH_2OH$	$C_6H_5CH=CHCH_2OAc$	10	90
20	$C_6H_5CH_2CH_2OH$	$C_6H_5CH_2CH_2OAc$	10	92
21	$CH_3CH(C_6H_5)CH_2OH$	$CH_3CH(C_6H_5)CH_2OAc$	12	88
22	$(C_6H_5)CH_2CH_2CH_2OH$	$(C_6H_5)CH_2CH_2CH_2OAc$	10	90
23	$CH_3(CH_2)_5CHOHCH_3$	$CH_3(CH_2)_5CH(OAc)CH_3$	12	87[d]
24	$CH_3(CH_2)_5CH_2OH$	$CH_3(CH_2)_5CH_2OAc$	10	88[d]
25	*cyclo*-$C_6H_{11}OH$	*cyclo*-$C_6H_{11}OAc$	10	85[d]
26	$(C_6H_5)_3C$-OH	$(C_6H_5)_3C$-OAc	20	80
27	$C_6H_5CHOHCH_2OH$	$C_6H_5CH(OAc)CH_2OAc$	12	85
28	CH_2OHCH_2OH	$CH_2(OAc)CH_2OAc$	14	86
29	(+)-Menthyl alcohol	(+)-Menthyl acetate	10	86[d]
30	C_6H_5OH	C_6H_5OAc	25	88
31	4-Me-C_6H_4OH	4-Me-C_6H_4OAc	18	92
32	4-Cl-C_6H_4OH	4-Cl-C_6H_4OAc	22	90
33	2,4-$(Cl)_2C_6H_3OH$	2,4-$Cl_2C_6H_3OAc$	18	90
34	4-NO_2-C_6H_4OH	4-NO_2-C_6H_4OAc	28	86
35	2,4-$(NO_2)_2C_6H_3OH$	2,4-$(NO_2)_2C_6H_3OAc$	30	80
36	1-Naphthol	1-Naphthyl acetate	24	86
37	C_6H_5SH	C_6H_5SAc	26	82
38	4-HO-C_6H_4OH	4-AcO-C_6H_4OAc	28	86

[a] Reaction conditions: substrate (5 mmol), acetic anhydride (one equiv. per OH), catalyst (1.32 mol %), solvent-free at r.t.
[b] All products were characterized on the basis of GC-MS, IR and ^{1}H-NMR spectral data and comparison with those of authentic samples or reported data.
[c] Isolated yield on the basis of the weight of the pure product obtained.
[d] GC-MS yields.

The general efficiency of this reaction was evident from the variety of hydroxy compounds including benzylic alcohols and primary, secondary and tertiary alcohols which react in excellent yields and short times.

The acetylation of a wide range of ring-substituted primary benzyl alcohols having various electron-donating and electron-withdrawing groups was investigated with acetic anhydride over $H_6GeW_{10}V_2O_{40}.22H_2O$ catalyst. These alcohols were efficiently converted to their corresponding acetates with excellent yields and the nature of the substituents had no significant effect on the reaction (Table 2, entries 1-12). 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. Also, various secondary alcohols were converted with high selectivity to their corresponding acetates (Table 2, entries 13-18). The unsaturated alcohol such as cinnamyl alcohol was selectively converted to the corresponding acetate and the carbon–carbon double bond remained intact under the reaction conditions (Table 2, entry 19). Aliphatic and non-benzylic alcohols were also converted into the corresponding acetate compounds with high efficiency under the same reaction conditions (Table 2, entries 20-25). It is noteworthy that sterically hindered tertiary alcohols, such as triphenylmethanol, also can be acetylated with high yield but it takes a longer reaction time (Table 2, entry 26). As shown by GC–MS analysis, there was no elimination product in the mixture. The efficacy of the catalyst is clearly evident in the acetylation of di-hydroxy compounds under similar conditions (Table 2, entries 27 and 28). It is noteworthy that in the case of optically active alcohol, the reaction proceeded well with retention of configuration (Table 2, entry 29).

Among the various hydroxy groups studied, the benzylic OH group was found to be the most reactive. As we can see from Table 3, functional groups such as -OMe, -CHO, -COMe, -CN and -NO_2 remained unchanged under the reaction conditions. Also, the conversion of benzyl alcohol to benzyl acetate on a 100 mmol scale proceeded just as well as the 5 mmol reaction (22 min, 95%).

The scope of this reaction was further extended for the acetylation of phenols (Table 2, entries 30-38). Phenol and differently substituted phenols were acetylated with quantitative yields after a prolonged reaction time in comparison with alcohols. The excellent activity of HPA was demonstrated by the high yields obtained for phenols that have electron-withdrawing groups (Table 2, entries 37 and 38).

It is evident from Table 2 that the phenols reacted slower than the alcohols and required longer reaction times. So, the selective interamolecular and intermolecular acetylation of an alcoholic OH group in the presence of a phenolic OH group could be achieved by the appropriate choice of reaction time. For example, *p*-hydoxybenzyl alcohol gave only *p*-hydroxybenzyl acetate with 92% isolated yield after a very short reaction time (10 min) at room temperature. Also, when a mixture of benzyl alcohol and phenol was stirred for 12 min in the presence of $H_6GeW_{10}V_2O_{40}.22H_2O$ under our reaction conditions, the alcohol was converted to its corresponding acetate with 90% GC yield while the phenol remained unchanged.

In order to confirm the reusability of $H_6GeW_{10}V_2O_{40}.22H_2O$ catalyst, after the first use in the acetylation of benzyl alcohol, it was separated from the reaction mixture and washed with ethyl acetate. The recovered catalyst was found to be reusable for four cycles without significant loss in activity (Table 3). At the same time, the concentrations of W and V in the filtrate

Table 3. Reusability of the catalyst for the acetylation of benzyl alcohol [a].

Cycle	0	1st	2nd	3rd	4th
Time (min)	8	8	10	10	10
Yield (%)[b]	92	91	88	87	88

[a] Reaction conditions: benzyl alcohol (5 mmol), Ac_2O (5 mmol), catalyst (1.32 mol %), without solvent at r.t.
[b] Isolated yields.

Table 4. Results of the acylation of benzyl alcohol with various anhydrides catalyzed by $H_6GeW_{10}V_2O_{40}.22H_2O$ [a].

Anhydride	Ac_2O	$(EtCO)_2O$	(*iso*-$PrCO)_2O$	(*tert*-$BuCO)_2O$	$(PhCO)_2O$[c]
Time (min)	8	14	20	30	35
Yield (%)[b]	92	90	87	85	82

[a] Reaction conditions: benzyl alcohol (5 mmol), Ac_2O (5 mmol), catalyst (1.32 mol %), without solvent at r.t.
[b] Isolated yield of the corresponding acylated product.
[c] Two equivalents of $(PhCO)_2O$ were used.

Table 5. Comparison of the results obtained for the acetylation of benzyl alcohol in the present work with those obtained by some reported catalysts.

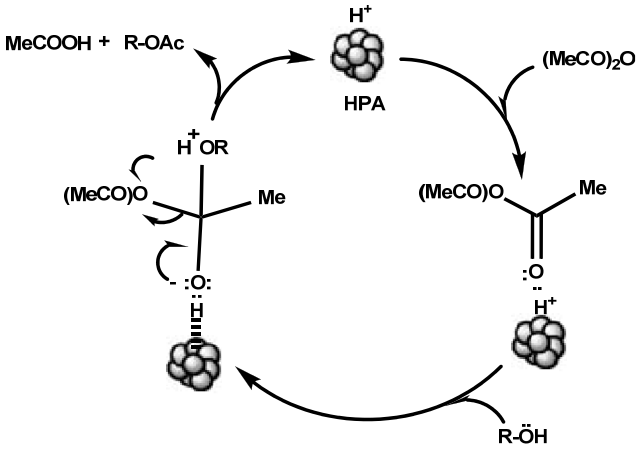
Entry	Catalyst	Conditions	Alcohol:Ac_2O (Mole ratio)	Catalyst (mol %, g)	Time	Yield (%)	Reference
1	$RuCl_3$	In CH_2Cl_2, rt	1:2	0.5	30 min	91	[17]
2	SiO_2/H_2SO_4	In CH_2Cl_2, rt	1:2	0.2 g	4 h	90	[18]
3	Mont. KSF	Solvent-free, rt	1:2	0.1 g	1 h	90	[19]
4	Distannoxane	In FC-72, rt	1:1	5	6 h	98	[25]
5	FER zeolite	Solvent-free, 75 °C	1:1.5	0.15 g	2 h	91	[26]
6	$ZrOCl_2.8H_2O$	In CH_2Cl_2, rt	1:2	0.5	5 min	94	[27]
7	ZrO_2-SO_4^{2-}	Solvent-free, rt	1:1	0.05 g	10 min	93	[35]
8	$Mg(ClO_4)_2$	Solvent-free, 0 °C	1:1	5	15 min	100	[30]
9	$Ce(OTf)_3$	In CH_3CN, rt	1:1.5	1	12 min	98	[18]
10	$H_6GeW_{10}V_2O_{40}$	Solvent-free, rt	1:1	1.32	8 min	92	This work

were determined to be less than 1% by ICP-AES. 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 the catalyst did not take place under the reaction conditions.

The activity of $H_6GeW_{10}V_2O_{40}.22H_2O$ as a general catalyst was tested via acylation of benzyl alcohol with various anhydrides under same reaction conditions (Table 4). In comparison with acetic anhydride, the reactions with higher anhydrides took longer times at room temperature. However, the reactions were completed in 14-35 min under solvent-free conditions, providing excellent yields (82-90%) of the corresponding acylated derivatives, It seemed that the rate of acylation was influenced by the steric and electronic factors of anhydrides and followed the order Ac_2O > $(EtCO)_2O$ > (iso-$PrCO)_2O$ > (*tert*-$BuCO)_2O$ > $(PhCO)_2O$. The longer times (10-20 min) required for the reaction with $(EtCO)_2O$, (iso-$PrCO)_2O$ and (*tert*-$BuCO)_2O$ were mainly due to the steric effect of the alkyl groups of these. The longer reaction time and the requirement of two equivalents of $(PhCO)_2O$ against one equivalent of Ac_2O were due to the combined effect of the steric and electronic factors of the phenyl group in $(PhCO)_2O$. The phenyl group makes the carbonyl group in $(PhCO)_2O$ less electrophilic due to the resonance effect.

In order to show the advantage of the present method, we have compared the obtained results in the acetylation of benzyl alcohol with acetic anhydride by $H_6GeW_{10}V_2O_{40}.22H_2O$ with some reported catalysts in the literature (Table 5). It is clear that with respect to the reaction conditions, substrate:Ac_2O mole ratio, reaction time, and/or product yield, the present method is more suitable and/or superior. We can see that reaction in the presence of most these catalysts required longer reaction time. Other advantages of catalyst in this work in comparison with other previously reported catalysts are: easy preparation, no moisture sensitivity, no explosive and expensive, and its very low toxicity.

In contrast to polyprotic inorganic acids, e.g., sulfuric acid and phosphoric acid which the dissociation of their hydrogen atoms occurs in a stepwise manner, the six protons of $H_6GeW_{10}V_2O_{40}.22H_2O$ were dissociated simultaneously [48]. This is probably due to a discrete ionic structure of solid HPAs, comprising fairly mobile basic structural units-hetero polyanion ($GeW_{10}V_2O_{40}^{6-}$) and countercations (H^+, H_3O^+ and $H_5O_2^+$) [41]. This unique structure manifests itself by exhibiting an extremely high proton mobility and very strong Brönsted acidity. On the other hand, heteropolyanions can stabilize cationic organic intermediates. According to these facts, the activation of carbonyl group in acetic anhydride takes place by coordinating with the protons on the surfaces of $H_6GeW_{10}V_2O_{40}.22H_2O$ particles. The reaction of alcohol or phenol with the activated carbonyl group resulted in the acetylated product and acetic acid (Scheme 1).



Scheme 1. The proposed catalytic cycle for the acetylation reaction over solid $H_6GeW_{10}V_2O_{40}.22H_2O$.

4. Conclusion

In conclusion, we have investigated the application of a V-containing HPA as the green and recyclable heterogeneous catalyst for the acetylation of alcohols and phenols with acetic anhydride under solvent-free conditions. Various hydroxy groups can be efficiently converted into their corresponding acetates with very short reaction times. It is noteworthy that the catalyst can be used for subsequent cycles of the acetylation without observable loss of activity. In contrast to many other acids, the storage of this non-hygroscopic and non-corrosive solid heteropoly acid does not require special precautions, e.g., it can be stored on a bench top for months without losing its catalytic activity.

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