**H$_6$GeMo$_{10}$V$_2$O$_{40}$·16H$_2$O Nanoparticles Prepared by Hydrothermal Method: A New and Reusable Heteropoly Acid Catalyst for Highly Efficient Acetylation of Alcohols and Phenols under Solvent-Free Conditions**

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Um novo ácido heteropolimetálico do tipo Keggin, H$_6$GeMo$_{10}$V$_2$O$_{40}$·16H$_2$O, foi sintetizado na forma de nanopartículas (5-8 nm) pelo método hidrotérmico e caracterizado por análise elementar, análise termogravimétrica (TGA), difratometria de raios X de pó (XRD), espectroscopia de infravermelho com transformada de Fourier (FTIR), espectroscopia UV-Visível, microscopia eletrônica de varredura (SEM), microscopia eletrônica de transmissão (TEM) e titulação potenciométrica. O ácido H$_6$GeMo$_{10}$V$_2$O$_{40}$·16H$_2$O revelou alta atividade catalítica na acetilação de diferentes alcoóis e fenóis com anidrido acetônico à temperatura ambiente (298 ± 2 K) e na ausência de solventes. O catalisador pode ser facilmente recuperado e usado repetidamente por 5 ciclos com pequena perda de sua atividade. A atividade catalítica do H$_6$GeMo$_{10}$V$_2$O$_{40}$·16H$_2$O foi maior do que a de outros ácidos heteroatômicos do tipo Keggin como H$_3$PW$_{12}$O$_{40}$, H$_3$PMo$_{12}$O$_{40}$ e H$_4$SiW$_{12}$O$_{40}$.

A new Keggin-type heteropoly acid, namely decamolybdodivanadogermanic acid (H$_6$GeMo$_{10}$V$_2$O$_{40}$·16H$_2$O), with nanosized particles (5-8 nm), has been synthesized by a hydrothermal method and characterized by elemental analysis, thermogravimetric analysis (TGA), powder X-ray diffractometry (XRD), Fourier-transform infrared spectroscopy (FTIR), UV-Visible spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and potentiometric titration. H$_6$GeMo$_{10}$V$_2$O$_{40}$·16H$_2$O revealed high catalytic activity for acetylation of various alcohols and phenols with acetic anhydride at room temperature (298 ± 2 K) and under solvent-free conditions. The catalyst can be easily recovered and used repeatedly for five cycles with a slight loss of activity. The catalytic activity of H$_6$GeMo$_{10}$V$_2$O$_{40}$·16H$_2$O was higher than that of other Keggin-type heteropoly acids, such as H$_3$PW$_{12}$O$_{40}$, H$_3$PMo$_{12}$O$_{40}$ and H$_4$SiW$_{12}$O$_{40}$.

**Keywords**: heteropoly acid, nanoparticles, acetylation, alcohols, solvent-free conditions

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**Introduction**

Acetylation is an efficient route for protecting the OH functional group of alcohols and phenols during oxidation, peptide coupling and glycosidation reactions.$^1$ This important transformation is typically performed using acetic anhydride and/or acetyl chloride in the presence of either basic or acidic catalysts. Numerous methodologies are available for this transformation,$^{2-17}$ but most of them are homogeneous and the catalysts are 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, the requirement for excess reagents or catalysts and the use of explosive, moisture-sensitive or expensive catalysts.

The use of heterogeneous catalysts seems one of the most promising solutions to avoid the above-mentioned problems.$^{18}$ Heterogeneous catalysts offer several advantages over homogeneous systems with respect to easy recovery, recycling and minimization of undesired toxic wastes. In this framework, several heterogeneous systems, including transition metal oxides,$^{19}$ montmorillonites,$^{20}$ HClO$_4$/SiO$_2$,$^{21}$ H$_2$SO$_4$/SiO$_2$,$^{22}$ AlPW$_{12}$O$_{40}$,$^{23}$ zeolites,$^{24}$ HBF$_4$/SiO$_2$,$^{25}$ MoO$_3$/Al$_2$O$_3$,$^{26}$ NaHSO$_4$/SiO$_2$,$^{27}$ sulfated zirconia,$^{28}$ (NH$_4$)$_2$H$_2$PW$_{12}$O$_{40}$,$^{29}$ silica-bonded cobalt(II) salen,$^{30}$ silica-bonded N-propyl sulfamic and S-propyl sulfuric acids,$^{31}$ have been applied as heterogeneous catalysts for the acetylation of alcohols and phenols. However, each of these methods has advantages and limitations.

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Heterogeneous acid catalysis by heteropoly acids (HPAs) has attracted much interest because of its potential for great economic rewards and green benefits. Unlike metal oxides and zeolites, HPAs possess very strong Brønsted 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 reactions, we report herein on the hydrothermally-assisted preparation of a new, nanosized V-substituted HPA (H₅GeMo₁₀V₂O₄₀•16H₂O) and its application as an efficient and recyclable heterogeneous catalyst for the 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 synthesis of HPA nanoparticles by the hydrothermal method and their catalytic application for the acetylation reaction.

**Experimental**

**Materials and methods**

Tungsten, vanadium and germanium contents were analyzed by ICP spectrometric method. The water content was determined by thermogravimetric analysis using a STA 449C thermal analyzer. The X-ray diffraction patterns were measured on a Bruker D8 Advance X-ray diffractometer with Cu Kα (λ = 1.5418 Å) radiation. A digital automatic potentiometric titrator apparatus (Model: VPT-MG, India) was used for the titration of HPA. The UV-Vis spectra were recorded on a Shimadzu UV-Vis recording spectrophotometer accessory in the 190-400 nm range with a resolution of 2 nm. Infrared spectra were recorded on a Shimadzu FTIR 8400 spectrometer in the 400-450 cm⁻¹ range with a resolution of 4 cm⁻¹ (compressed pellets of 1 mg of catalysts and 100 mg KBr). The morphology of the catalyst was determined by scanning electron microscopy (SEM, Philips XL-30) and transmission electron microscopy (TEM, LEO-906E).

Samples for TEM were prepared by deposition of HPA in EtOH solution onto a standard Cu grid covered with a holey carbon film.

**Preparation of the H₅GeMo₁₀V₂O₄₀•16H₂O catalyst**

The H₅GeMo₁₀V₂O₄₀•16H₂O catalyst was synthesized via application of (A) and (B) solutions as follows.

**Solution (A):** 50 mL of sodium metavanadate dihydrate (NaVO₂•2H₂O, 15.6 g, 100 mmol) was mixed with 20 mL of sodium molybdate dihydrate (Na₂MoO₄•2H₂O, 6.05 g, 25 mmol) under heating. After cooling the resulting solution to room temperature, its pH was adjusted to 2.5 with concentrated sulfuric acid to give a red solution.

**Solution (B):** 100 mL of sodium molybdate dihydrate (Na₂MoO₄•2H₂O, 54.45 g, 225 mmol) was mixed with 67.6 mL of the alkaline germanate stock solution ([Ge] = 0.37 mol L⁻¹). The pH of the mixture was adjusted to 6 with sulfuric acid.

Solution (B) was added dropwise to solution (A) with vigorous stirring while the pH was kept at 2.5. The final mixture was transferred into an autoclave and heated at 423 K for 2 h. After cooling the mixture to room temperature, it was extracted with 500 mL of diethyl ether. The evaporation in air resulted in the H₅GeMo₁₀V₂O₄₀•16H₂O as a crystalline, orange-red solid product (40.31 g, 78%). Elemental analysis found: Ge, 3.49; Mo, 46.44; V, 4.89; H₂O, 13.93%. FTIR (KBr) vₗυ/cm⁻¹: 3500 (O–H), 1620 (O–H), 955 (M–O–M), 810 (Ge–O–M) and 590 (O–Ge–O), (M = Mo and V; O, inner oxygen; Oₐ, corner-shared oxygen; Oₑ, edge-shared oxygen; Oₐₑ, terminal oxygen). UV spectrum (λᵥmax/nm, CH₂CN): 205 (O → M CT); 258.5 (O → M CT).

**Catalytic tests**

The acetylation of alcohols and phenols with acetic anhydride as the acetylating agent was carried out at room temperature (298 ± 2 K) in a glass thermostated vessel equipped with a stirrer. The reactor was charged with a mixture of alcohol or phenol (20 mmol), acetic anhydride (20 mmol) and H₅GeMo₁₀V₂O₄₀•16H₂O (0.15 g, 0.36 mol% based on the alcoholic or phenolic substrate). The progress of the reaction was monitored by thin layer chromatography (TLC) and/or gas chromatography-mass spectrometry (GC-MS). The catalyst was separated by addition of ethyl acetate (2 × 20 mL) to the reaction mixture. The filtrate was washed with 15 mL of a 10% aqueous solution of NaHCO₃ and dried under Na₂SO₄. The solvent was removed under reduced pressure to give the product. The results are shown in Table 3. All products were identified by comparing their physical and spectral data (mp, TLC, FTIR, ¹H NMR and GC-MS) with known samples or literature data.

**Recycling tests**

After each run, the catalyst was separated by adding ethyl acetate to the reaction mixture. The recovered catalyst was dried and then reused (Table 5).
Results and Discussion

Characterization of H$_6$GeMo$_{10}$V$_2$O$_{40}$

Initially, nanosized HPA catalyst was prepared by a hydrothermal-assisted method and characterized by various techniques including elemental analysis, TGA, FTIR, XRD, UV-Vis spectroscopy and potentiometric titration. The thermogravimetric analysis of HPA is shown in Figure 1. The first weight loss at 323-383 K was attributed to the evaporation of physically adsorbed water. The second weight loss step occurred in the temperature range of 423-653 K, corresponding to the loss of chemically adsorbed water molecules. The percent of weight loss of this step was about 14%, which is consistent with the theoretical weight loss (13.93%) calculated for the formation of the HPA molecule with 16 molecules of water. The weight loss observed at 693-973 K can be attributed to the decomposition of Keggin anions.

The FTIR spectrum of HPA is shown in Figure 2. The characteristic bands of HPA with Keggin structure appeared in the range of 500-1000 cm$^{-1}$. Also, the bands related to the stretching and bending vibrations of the crystalline water molecules are observed around 3500 and 1620 cm$^{-1}$, respectively.

X-ray powder diffraction analysis is widely used to study the structural features of HPA and explain their properties. The X-ray powder diffraction of the obtained HPA is shown in Figure 3. The diffraction peaks at 20 (in degree) = 8-11, 18-22, 24-30 and 33-40 are characteristic of HPA anions with Keggin structure. The average particle size was calculated by X-ray diffraction line broadening using the Debye-Scherrer equation:

$$d = \frac{(0.89 \lambda)}{(h_{1/2} \cos \theta)}$$

where $d$ represents the grain size; $\lambda$ is the wavelength of the X-ray (Cu K$_\alpha$, 0.15418 nm); $\theta$ is the diffraction angle of the peak and $h_{1/2}$ stands for the full-width at half-height of the peaks. The particle sizes calculated using the intense peaks at 20 (in degree) = 8, 21, 25.5 and 35 were 7.6, 7.4, 8.2 and 8 nm, respectively. These values are in accordance with TEM observation (vide infra).

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. As we can see in Figure 4, the UV-Vis spectrum of the catalyst shows two characteristic bands at 205 and 258.5 nm. Combined with FTIR spectra and XRD diffratogram, this result confirms that the HPA possesses Keggin structure.

The number of protons in the HPA molecule and their ionization states can be determined by potentiometric titration. In the potentiometric titration curve (Figure 5), the [OH]/[HPA] ratio is about 6 at the end point, which shows that there are six protons in the HPA and that the
electric charge of the heteropoly anion is six. This finding confirms that the protons of the HPA are equivalent and are dissociated in one step. This property is beneficial to its catalytic activity.

![Figure 5](image5.png)

**Figure 5.** The potentiometric titration curve of the HPA catalyst.

Figure 6 shows the SEM and TEM images of the HPA powder. The SEM image reveals that the powder is composed of aggregated, extremely fine semi-spherical particles. This observation indicates that the HPA powder is a crystalline aggregate of nanoparticles. The TEM image confirms that the HPA particles have a narrow size distribution in a range from 5 to 8 nm with the mean particle size of about 6.5 nm. The particle size determined by TEM is close to the particle size calculated by the Debye-Scherrer’s formula from the XRD pattern.

![Figure 6](image6.png)

**Figure 6.** SEM and TEM images registered for the HPA catalyst (× 50000).

**Catalytic activity of \( \text{H}_6\text{GeMo}_{10}\text{V}_2\text{O}_{40} \)**

In the second part of this study, the activity of \( \text{H}_6\text{GeMo}_{10}\text{V}_2\text{O}_{40}\cdot16\text{H}_2\text{O} \) nanoparticles as a new heterogeneous HPA catalyst was investigated on the acetylation reaction of alcohols and phenols. Initial experiments were focused on the acetylation of benzyl alcohol as a model substrate to check the catalytic activity of this HPA and to optimize the reaction conditions.

**Effect of the amount of catalyst**

In a typical reaction, a mixture of benzyl alcohol (20 mmol) and acetic anhydride (20 mmol) was stirred in the presence of different amounts of the nanosized HPA catalyst under solvent-free conditions at room temperature. The progress of the reaction was monitored by TLC. To optimize the catalyst requirement, the amount of catalyst was changed from 0.12 to 0.72 mol% with respect to the amount of benzyl alcohol. As shown in Table 1, the yield of benzyl acetate was increased with the increase of the amount of catalyst from 0.12 to 0.36 mol%, which is due to the proportional increase in the number of active sites on the surface of the catalyst nanoparticles (Table 1, entries 1-4). However, no significant improvement in the yield was observed with higher loads (Table 1, entries 5 and 6). The optimum amount of catalyst in the reaction mixture was 0.36 mol% with respect to the alcohol, which resulted in the best yield. The essential role played by the catalyst is evident from the extremely low yield of benzyl acetate found in the absence of the catalyst (Table 1, entry 7).

**Table 1.** Effect of the amount of catalyst on the reaction of benzyl alcohol with acetic anhydride

| entry | Catalyst / mol% | time / min | Yield / % |
|-------|-----------------|------------|-----------|
| 1     | 0.12            | 4          | 11        |
| 2     | 0.18            | 4          | 16        |
| 3     | 0.24            | 4          | 38        |
| 4     | 0.36            | 4          | 96        |
| 5     | 0.48            | 4          | 95        |
| 6     | 0.72            | 4          | 95        |
| 7     | 0               | 30         | trace     |

*Reaction conditions: benzyl alcohol (20 mmol), acetic anhydride (20 mmol), without solvent, at room temperature (r.t.).

**Effect of the solvent nature**

In order to choose the best medium, we also tested the effect of solvents such as acetonitrile, toluene, dichloromethane, chloroform and tetrahydrofuran (thf) in the reaction. According to Table 2, the yield of product was lower in homogeneous systems (CH₃CN and thf) comparing to heterogeneous systems (toluene, dichloromethane,
chloroform). The low yield in toluene is very likely explained by the side reactions between toluene and the acetylation agent. However, the best results in terms of time and yield have been achieved without the use of any solvent. So, we have continued the reactions under solvent-free conditions. Generally, the reduction of the activity of catalyst in the presence of solvent and in homogeneous systems could be attributed to the existence of various interactions, e.g., solvation and/or complex formation with the reactants and/or catalyst. When the reaction mixture is stirred without a solvent, these interactions or interferences are eliminated, so that the higher efficiency of the catalytic system could be achieved, probably through increasing the number of effective collisions between reactants and catalyst.

**Table 2.** Effect of the solvent on the reaction of benzyl alcohol with acetic anhydride catalyzed by $H_4GeMo_{10}V_2O_{40}•16H_2O$.

| entry | Solvent         | time / min | Yield / % |
|-------|-----------------|------------|-----------|
| 1     | acetonitrile    | 60         | 56        |
| 2     | toluene         | 60         | 40        |
| 3     | dichloromethane | 60         | 75        |
| 4     | chloroform      | 60         | 64        |
| 5     | tetrahydrofuran | 60         | 55        |
| 6     | without solvent | 4          | 96c       |

*Reaction conditions: benzyl alcohol (20 mmol), acetic anhydride (20 mmol), catalyst (0.36 mol%), solvent (10 mL) at room temperature; GC-MS yields; cisolated yields.

**Effect of the reagent nature**

To show the generality and scope of this procedure, we studied the acetylation of various alcohols, such as primary, secondary and tertiary alcohols, as well as allylic alcohol and diols. The results in Table 3 show that all alcohols were selectively converted to the corresponding acetates in quantitative yields without any evidence of the formation of side products. The general efficiency of this catalytic system was evident from the variety of hydroxy compounds that were acetylated with excellent yields and within short reaction 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 the $H_4GeMo_{10}V_2O_{40}•16H_2O$ catalyst. These alcohols and also primary aliphatic alcohols were efficiently converted to their corresponding acetates with excellent yields and the nature of the substituents had no significant effect on the reaction times and yields (Table 3, entries 1-18). The $\alpha,\beta$-unsaturated primary alcohol (cinnamyl alcohol) was selectively converted to the corresponding acetate, and the carbon-carbon double bond remained intact under the reaction conditions (Table 3, entry 19). Also, various secondary alcohols were converted with high selectivity to their corresponding acetates with high efficiency under the same reaction conditions (Table 3, entries 20-24). Sterically hindered tertiary alcohols such as triphenylmethanol can also be acetylated with high yield, but it takes longer (Table 3, entry 25). As shown by GC-MS analysis, there was no elimination product in the mixture. The efficacy of the catalyst can be seen clearly in the acetylation of di-hydroxy compounds under similar conditions (Table 3, entries 26 and 27). Cyclic alcohols were also converted into the corresponding acetate compounds with high efficiency (Table 3, entries 28-29).

It is very interesting that in the case of an optically active cyclic alcohol, the reaction proceeded well with the retention of configuration (Table 3, 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 $-OMe$, $-CHO$, $-CO_{Me}$, $-CN$ and $-NO_2$ remained unchanged under the reaction conditions. Also, the conversion of benzyl alcohol into benzyl acetate on a 100 mmol scale proceeded just as well as the 20 mmol reaction (10 min, 95%).

The scope of this reaction was further extended for the acetylation of phenols. Phenol, substituted phenols, hydroquinone, 1-naphthol and thiophenol were acetylated with quantitative yields after longer reaction times in comparison with alcohols (Table 3, entries 30-38). The excellent activity of HPA was demonstrated by the high yields obtained for phenols having electron-withdrawing groups (Table 3, entries 34 and 35).

The acetylation of phenols was slower than that of alcohols and required longer reaction times, so that the selective intramolecular 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, the reaction of 4-hydroxybenzyl alcohol with one equivalent of acetic anhydride gave only 4-hydroxybenzyl acetate with 94% yield after a very short reaction time (5 min) at room temperature. Indeed, when an equimolar mixture of benzyl alcohol and phenol was subjected to acetylation reaction in the presence of $H_4GeMo_{10}V_2O_{40}•16H_2O$ under the present reaction conditions, the alcohol was converted to its corresponding acetate with 96% yield after stirring for 5 min while the phenol remained unchanged. These results show the high selectivity of our method.

The activity of $H_4GeMo_{10}V_2O_{40}•16H_2O$ as a general catalyst was tested via acylation of benzyl alcohol with various anhydrides under the same reaction conditions (Table 4). In comparison with acetic anhydride, the reactions with higher anhydrides took longer times at
Table 3. Results of the acetylation of alcohols and phenols with acetic anhydride catalyzed by H₂GeMo₉V₃O₄₋₁₆H₂O⁺

| Entry | Substrate         | Product²b | time / min | Yield / %³ |
|-------|-------------------|-----------|------------|------------|
| 1     | C₆H₅CH₂OH         | C₆H₅CH₂OAc| 4          | 96         |
| 2     | 4-Pr-C₆H₅CH₂OH    | 4-Pr-C₆H₅CH₂OAc| 3.5       | 97         |
| 3     | 4-MeO-C₆H₅CH₂OH   | 4-MeO-C₆H₅CH₂OAc| 3          | 95         |
| 4     | 3-MeO-C₆H₅CH₂OH   | 3-MeO-C₆H₅CH₂OAc| 4          | 93         |
| 5     | 4-Br-C₆H₅CH₂OH    | 4-Br-C₆H₅CH₂OAc| 4.5       | 92         |
| 6     | 2,4-(Cl)₂-C₆H₅CH₂OH| 2,4-(Cl)₂-C₆H₅CH₂OAc| 5        | 94         |
| 7     | 2-Cl-C₆H₅CH₂OH    | 2-Cl-C₆H₅CH₂OAc| 6          | 92         |
| 8     | 4-NO₂-C₆H₅CH₂OH   | 4-NO₂-C₆H₅CH₂OAc| 6          | 95         |
| 9     | 2-NO₂-C₆H₅CH₂OH   | 2-NO₂-C₆H₅CH₂OAc| 6.5       | 90         |
| 10    | 3-NO₂-C₆H₅CH₂OH   | 3-NO₂-C₆H₅CH₂OAc| 5.5       | 94         |
| 11    | 4-CF₃-C₆H₅CH₂OH   | 4-CF₃-C₆H₅CH₂OAc| 6          | 92         |
| 12    | 4-CN-C₆H₅CH₂OH    | 4-CN-C₆H₅CH₂OAc| 6          | 90         |
| 13    | 3-CHO-C₆H₅CH₂OH   | 3-CHO-C₆H₅CH₂OAc| 7          | 86         |
| 14    | 3-MeCO-C₆H₅CH₂OH  | 3-MeCO-C₆H₅CH₂OAc| 7          | 84         |
| 15    | C₆H₅CH₂CH₂OH      | C₆H₅CH₂CH₂OAc| 4.5       | 94         |
| 16    | CH₃CH(C₆H₅CH₂OH)  | CH₃CH(C₆H₅CH₂OAc)| 5         | 94         |
| 17    | (C₆H₅CH₂CH₂CH₂OH) | (C₆H₅CH₂CH₂CH₂OAc)| 5        | 90         |
| 18    | CH₃(CH₃)₂CH₂OH    | CH₃(CH₃)₂CH₂OAc| 8          | 88⁴       |
| 19    | C₆H₅CH=CHCH₂OH    | C₆H₅CH=CHCH₂OAc| 4.5       | 92         |
| 20    | C₆H₅CHOHCH₂H₂     | C₆H₅CHOHCH₂H₂| 4.5       | 96         |
| 21    | C₆H₅CHOHOHCH₂H₂   | C₆H₅CHOHOHCH₂H₂| 4          | 95         |
| 22    | CH₃(CH₃)₂CHOHCH₂H₂| CH₃(CH₃)₂CHOHCH₂H₂| 8       | 86⁵       |
| 23    | (C₆H₅)₂CHOH       | (C₆H₅)₂CHOH| 5          | 94         |
| 24    | C₆H₅C(=O)CHOHCH₂H₂| C₆H₅C(=O)CHOHCH₂H₂| 6         | 89         |
| 25    | (C₆H₅)₂C-CH₂OH    | (C₆H₅)₂C-CH₂OAc| 14         | 86         |
| 26    | C₆H₅CHOHCH₂OH     | C₆H₅CHOHCH₂OH| 8          | 82         |
| 27    | CH₃OHCH₂OH        | CH₃OHCH₂OH| 8          | 87         |
| 28    | cyclo-C₆H₅OH      | cyclo-C₆H₅OH| 10         | 85⁶       |
| 29    |                     |           | 7          | 86⁶       |
| 30    | C₆H₅OH            | C₆H₅OAc| 22         | 90         |
| 31    | 4-Me-C₆H₅OH       | 4-Me-C₆H₅OAc| 15         | 94         |
| 32    | 4-Cl-C₆H₅OH       | 4-Cl-C₆H₅OAc| 18         | 92         |
| 33    | 2,4-(Cl)₂-C₆H₅OH  | 2,4-(Cl)₂-C₆H₅OAc| 24       | 90         |
| 34    | 4-NO₂-C₆H₅OH      | 4-NO₂-C₆H₅OAc| 26         | 88         |
| 35    | 2,4-(NO₃)₂-C₆H₅OH | 2,4-(NO₃)₂-C₆H₅OAc| 30       | 86         |
| 36    | HOC₆H₅OH          | AcO₆H₅OAc| 26         | 84         |
| 37    |                     |           | 22         | 90         |
| 38    | C₆H₅SH            | C₆H₅SHAc| 25         | 88         |

²Reaction conditions: substrate (20 mmol), acetic anhydride (one equiv. per OH), catalyst (0.36 mol%), solvent-free, room temperature; ³all products were characterized on the basis of GC-MS, IR and ¹H NMR spectral data and comparison with those of authentic samples or reported data; ⁴isolated yield on the basis of the weight of the pure product obtained; ⁵GC-MS yields.

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room temperature. However, the reactions were completed in 10-28 min under solvent-free conditions affording the corresponding acylated derivatives, providing excellent yields (86-91%). It seemed that the rate of acylation was influenced by the steric and electronic factors of anhydrides and followed the order Ac₂O > (EtCO)₂O > (i-PrCO)₂O > (t-BuCO)₂O > (PhCO)₂O. The longer times (10-20 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. The longer reaction time and the requirement of two equiv. of (PhCO)₂O against one equiv. of Ac₂O 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.

**Reusability and stability of the catalyst**

In order to confirm the reusability and stability of H₆GeMo₁₀V₂O₄₀•16H₂O catalyst, it was separated from the reaction mixture after its first use in the acetylation of benzyl alcohol and washed with ethyl acetate. The recovered catalyst was found to be reusable for five cycles with a slight loss in activity (Table 5). At the same time, the concentration of Mo in the filtrate was determined to be less than 1-1.5% by ICP-AES (inductively coupled plasma atomic emission spectroscopy). In one experiment, when the catalyst was separated from the reaction mixture 2 min after the beginning of the reaction and the filtrate was further stirred at room temperature, no extra formation of benzyl acetate was observed via GC-MS and TLC even after 25 min. On the other hand, the catalyst recovered in this experiment was used for recycling and its deactivation was not observed in the conversion of benzyl alcohol to benzyl acetate (4 min, 94%). Furthermore, the nature of the recovered catalyst after the fifth cycle was studied by elemental analysis, UV-Vis spectrophotometry and TEM. As shown in Figure 7, elemental analysis, UV-Vis spectrum and morphology of the recovered catalyst at the last cycle showed no observable changes compared to the fresh catalyst. All these findings confirm that the present reaction catalyzed by H₆GeMo₁₀V₂O₄₀•16H₂O is heterogeneous in nature and the catalyst is stable under the reaction conditions employed in this work.

**Table 4. Results of the acylation of benzyl alcohol with various anhydrides catalyzed by H₆GeMo₁₀V₂O₄₀•16H₂O**

| Anhydride   | Ac₂O | (EtCO)₂O | (i-PrCO)₂O | (t-BuCO)₂O | (PhCO)₂O |
|-------------|------|----------|------------|------------|----------|
| time / min  | 4    | 10       | 13         | 20         | 28       |
| Yield / %   | 96   | 91       | 88         | 88         | 86       |

*Reaction conditions: benzyl alcohol (20 mmol), anhydride (20 mmol), catalyst (0.36 mol%) at room temperature; isolated yield of the corresponding acylated product; two equivalents of (PhCO)₂O were used.

**Table 5. Reusability of the catalyst for the acetylation of benzyl alcohol with acetic anhydride**

| Cycle | Yield / % |
|-------|-----------|
| 0     | 96        |
| 1     | 94        |
| 2     | 90        |
| 3     | 90        |
| 4     | 91        |
| 5     | 88        |

*Reaction conditions: benzyl alcohol (20 mmol), Ac₂O (20 mmol), without solvent at room temperature.
Comparison of the activity of $\text{H}_2\text{GeMo}_{10}\text{V}_2\text{O}_{40}\cdot16\text{H}_2\text{O}$ with conventional Keggin-type heteropoly acids and some reported solid catalysts

The activity of $\text{H}_2\text{GeMo}_{10}\text{V}_2\text{O}_{40}\cdot16\text{H}_2\text{O}$ in the model reaction was compared with several Keggin-type HPAs with known water content including $\text{H}_3\text{PMO}_{12}\text{O}_{40}\cdot28\text{H}_2\text{O}$ (Fluka, 99%), $\text{H}_2\text{PW}_{12}\text{O}_{40}\cdot30\text{H}_2\text{O}$ (synthesized according to reference 34), $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot13\text{H}_2\text{O}$ (synthesized according to reference 34), $\text{H}_2\text{PW}_{13}\text{O}_{40}\cdot7\text{H}_2\text{O}$ (Merck, 99%), $\text{H}_2\text{SiW}_{12}\text{O}_{40}\cdot23\text{H}_2\text{O}$ (Fluka, 99%) and $\text{Na}_2\text{PW}_{12}\text{O}_{40}\cdot\text{H}_2\text{O}$ (Merck, 99%). The results listed in Table 6 show that, in terms of reaction time and product yield, our catalyst is superior. It is noteworthy to mention that three types of $\text{H}_2\text{PW}_{12}\text{O}_{40}n\text{H}_2\text{O}$ with different water contents ($n = 30, 13, 7$) gave similar results, indicating that the efficiency of catalyst was not affected by the water content. Also, we have used the Na$^+$ salt of $\text{H}_2\text{PW}_{12}\text{O}_{40}(\text{Na}_2\text{PW}_{12}\text{O}_{40}\times\text{H}_2\text{O})$ as a catalyst, and that was not effective. This finding confirms that Na$^+$ ions and also $\text{H}_2\text{O}$ do not participate in the reaction. Although it is difficult to offer an explanation for the different activities of 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.\(^\text{32}\) Also, the transition metal cations such as V$^{3+}$ have an important effect on the catalytic properties of these compounds when they substitute molybdenum cations in the octahedral Mo$^{6+}$ groups of the Keggin structure.\(^\text{32}\) Organic reagents can coordinate with V$^{3+}$-sites of the heteropoly anion and therefore change the charge density in the organic groups. Furthermore, the nanosized catalysts provide more contact surface for the reactants in comparison with the bulk catalysts. At this time, although the nano nature of the $\text{H}_2\text{GeMo}_{10}\text{V}_2\text{O}_{40}\cdot16\text{H}_2\text{O}$ nanoparticles has been confirmed by TEM and XRD techniques, we can not state that a nano size effect is responsible for the higher activity of this catalyst.

A comparison of the catalytic efficiency of $\text{H}_2\text{GeMo}_{10}\text{V}_2\text{O}_{40}\cdot16\text{H}_2\text{O}$ with selected, previously known catalysts is collected in Table 7. It is clear that with respect to the reaction conditions (substrate:Ac$_2$O mole ratio, reaction time) and/or product yield, the present method is superior. For example, the acetylation of benzyl alcohol in the presence of most listed catalysts takes longer time for completion.

The activity of the silver salt of the catalyst, Ag$_{\text{25}}\text{GeMo}_{10}\text{V}_2\text{O}_{40}$, 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. This test confirmed that the catalytic activity of the HPA arises mainly from its very strong Brønsted acidity. In contrast to polyprotic inorganic acids, e.g., sulfuric acid and phosphoric acid, which ionize in a stepwise manner, the ionization of the six protons of $\text{H}_2\text{GeMo}_{10}\text{V}_2\text{O}_{40}\cdot16\text{H}_2\text{O}$ was completed in one step (Figure 5). This is probably due to a discrete ionic structure of solid HPAs, comprising fairly mobile basic structural units, i.e., heteropolyanion ($\text{GeMo}_{10}\text{V}_2\text{O}_{40}x$) and counterions (e.g., H$^+$, H$_2$O and H$_2$O$_2^+$).\(^\text{32}\) This unique structure manifests itself by exhibiting an extremely high proton mobility and very strong Brønsted acidity. On the other hand, heteropolyanions can stabilize cationic organic intermediates. According to these facts, the activation of the carbonyl group in acetic anhydride takes place by coordination to the protons on the surface of the $\text{H}_2\text{GeMo}_{10}\text{V}_2\text{O}_{40}\cdot16\text{H}_2\text{O}$ nanoparticles. The activated carbonyl group is attacked by the OH group of the substrate.

### Table 6. Acetylation of benzyl alcohol catalyzed by different HPAs$^a$

| entry | HPA | time / min | Yield / %$^b$ |
|-------|-----|------------|---------------|
| 1     | $\text{H}_3\text{PMO}_{12}\text{O}_{40}\cdot28\text{H}_2\text{O}$ | 60 | 54 |
| 2     | $\text{H}_2\text{PW}_{12}\text{O}_{40}\cdot30\text{H}_2\text{O}$ | 60 | 63 |
| 3     | $\text{H}_2\text{PW}_{12}\text{O}_{40}\cdot13\text{H}_2\text{O}$ | 60 | 62 |
| 4     | $\text{H}_2\text{PW}_{13}\text{O}_{40}\cdot7\text{H}_2\text{O}$ | 60 | 62 |
| 5     | $\text{H}_2\text{SiW}_{12}\text{O}_{40}\cdot23\text{H}_2\text{O}$ | 60 | 52 |
| 6     | $\text{Na}_2\text{PW}_{12}\text{O}_{40}\times\text{H}_2\text{O}$ | 60 | trace |
| 7     | $\text{H}_2\text{GeMo}_{10}\text{V}_2\text{O}_{40}\cdot16\text{H}_2\text{O}$ | 4 | 92 |

$^a$Reaction conditions: benzyl alcohol (20 mmol), Ac$_2$O (20 mmol), HPA (0.36 mol%), without solvnet at room temperature; $^b$isolated yields.

### Table 7. Comparison of the results obtained for the acetylation of benzyl alcohol in the present work with those obtained by some reported solid catalysts

| entry | Solid catalyst | Conditions | Alcohol:Ac$_2$O (mole ratio) | Catalyst | time | Yield / % | Ref. |
|-------|---------------|------------|-----------------------------|----------|------|----------|------|
| 1     | Mont. KSF     | Solvent-free, r.t. | 1:2 | 0.1 g | 1 h | 90 | 20 |
| 2     | SiO$_2$/H$_2$SO$_4$ | In CH$_2$Cl$_2$, r.t. | 1:2 | 0.2 g | 4 h | 90 | 22 |
| 3     | FER zeolite   | Solvent-free, 75 °C | 1:1.5 | 0.15 g | 2 h | 91 | 24 |
| 4     | ZrO$_2$/SO$_4$ | Solvent-free, r.t. | 1:1 | 0.05 g | 10 min | 93 | 28 |
| 5     | (NH$_4$)$_2$HPO$_4$ | Solvent-free, r.t. | 1:1 | 0.5 mol% | 1 h | 92 | 29 |
| 6     | $\text{H}_2\text{GeMo}_{10}\text{V}_2\text{O}_{40}$ | Solvent-free, r.t. | 1:1 | 0.36 mol% | 4 min | 96 | This work |
which is a moderately reactive nucleophile, resulting in the formation of the corresponding acetate and acetic acid (Scheme 1).

![Scheme 1. Proposed catalytic cycle for the acetylation reaction over HPA.](image)

According to this mechanism, the higher reactivity of alcohols and the selective acetylation of an alcohol in the presence of a phenol could be related to the higher nucleophilicity of the oxygen atom of the alcoholic OH group.

**Conclusions**

A new V-containing HPA with nanosized particles was prepared by the hydrothermal process. The nano nature of its particles was confirmed by XRD and TEM results. This HPA was used as a new 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. The catalyst can be used for subsequent cycles of acetylation without observable loss of activity. For all the examples studied, this simple method eliminates completely the necessity of using organic solvents in the reaction.

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