

Dehydration of 1-propanol using $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as catalyst

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The activation of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ under different thermal conditions has been evaluated by calorimetry in acetonitrile solution using pyridine as a probe, and the results correlated to the dehydration of 1-propanol. Treatments at 200, 300, and 400 °C show substantial changes in the catalytic activity of 12-tungstophosphoric acid as a function of activation temperature and time. Analysis of the samples by XRD, FTIR, TGA and DSC was performed to determine structural changes and thermal stability of the heteropolytungstic acid.

Introduction

Acid catalysis involving heteropoly tungstophosphoric compounds has attracted much interest.^{1–3} Heteropolyanions such as $\text{PW}_{12}\text{O}_{40}^{3-}$ have very low negative charge on the surface oxygens, which make their acid forms, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (abbreviated as HPW), strong acids.⁴ HPW is known to have a primary and secondary structure. The primary structure comprises the P, W and O atoms. Twelve WO_6 octahedra surround a central PO_4 tetrahedron, which include four kinds of oxygen atoms. Four edge-shared units of W_3O_{13} are connected by corners accounting for the total amount of atoms in the anion. This arrangement is known as the Keggin structure (α type), and geometrical isomers (β and γ type) are also known.^{5–9} The secondary structure depends upon the degree of hydration and is formed by H^+ and H_2O molecules. A typical structure of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ is comprised of four polyanions of $\text{PW}_{12}\text{O}_{40}^{3-}$ connected by $\text{H}^+(\text{H}_2\text{O})_2$ bridges by hydrogen bonding at the terminal oxygens atoms of the anions.^{5–9}

Many studies have demonstrated the usefulness of HPW as an acid catalyst, being more effective than ordinary protonic acids.^{10–19} However, few have been done on the effects of calcination pretreatment on acidity and reactivity of HPW.²⁰ The primary Keggin structure is known to be stable up to 500 °C, and after that it decomposes to P_2O_5 and WO_3 . Significant changes are known to occur to the secondary structure at temperatures below that of decomposition. For example, HPW is capable of losing some lattice oxygen without collapsing its primary Keggin structure at 450 °C.¹¹ This is accomplished by some slight rearrangement of the secondary structure. The complete thermal decomposition of HPW has been studied.¹⁶ Changes to the secondary structure below 450 °C will affect not only the whole structure, but the acidity and reactivity of HPW. Therefore, the effect of pretreatment calcination is of interest.

Acidity determinations of a heterogeneous solid acid are most commonly done by use of Hammett indicators, and infrared analysis of an adsorbed base. Recently, these methods have come under criticism due to their inability accurately to determine the acid site number and strength for a solid acid.²¹ Other common measurements involve TPD (temperature-programmed desorption), and microcalorimetry of gaseous bases.²² More recently, a calorimetric method known as Cal-ad,²³ which involves measuring the heat of interaction between a probe base and the acid sites of the solid in a non-interacting solvent, has been used. This method was successful

in correlation of solid acidity to acid catalysed reactivity for different solid acids.^{24,25}

In this study the calorimetric method has been used to evaluate the acidity of the protons for HPW calcined at temperatures of 200, 300 and 400 °C for 2 hours in air. The results along with powder XRD, FTIR, TGA and DSC were correlated to the activity for dehydration of 1-propanol.

Experimental

Materials

Phosphotungstic acid (HPW) was obtained from the Aldrich chemical company, acetonitrile and pyridine from Fisher. Further purification of acetonitrile involved first drying over molecular sieves 4 Å for 24 hours, distilling over P_2O_5 , and finally storing over molecular sieves 4 Å in a dry bag. The solvent was used next day to avoid any water contamination. Pyridine was distilled over CaH_2 . A solution of pyridine in acetonitrile was prepared with both liquids dried, and stored in the dry bag. 1-Propanol used in the dehydration reaction was obtained from Aldrich and used as received. All the other reactants used were of analytical grade.

Calcination procedures

HPW was treated under a dry air flow at 200, 300 and 400 °C, during 2 hours, and 10 hours (300 °C), after each temperature had been reached. Then, calcined HPW was stored immediately in a dry box. The sample drying apparatus and technique has successfully been used to dry HZM-5 previously.²⁶

Calorimetric measurements

Samples of 0.4 g of calcined HPW were weighed inside the dry box, and transferred to an isothermal calorimetric cell containing a stirrer bar. All details of the calorimeter²³ and the calorimetric procedure¹⁸ were described previously.

1-Propanol dehydration

The reaction was carried out using a one-time flow through reactor over 0.5 g of the catalyst. Nitrogen was used as the carrier gas, which was passed over a saturator containing 1-propanol, heated to 90 °C. The pre and post gas samples were analysed by gas chromatography (Hewlett Packard model 5890).

Thermal analysis

DSC samples were analysed in a DuPont TA instruments model 2910 DSC using a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. TGA was obtained on the same instrument using 2950 module. Both experiments were performed using dry air as the purge gas.

Powder XRD and FTIR

Samples were scanned at 40 kV with a Philips X-ray diffractometer at 20.00 s deg^{-1} (Fig. 1) and a Rigaku D/MAX-2A/C with Cu-K α radiation at 40 kV and 30 mA (Fig. 2). A 2θ range of 5 to 50° was scanned. Infrared spectra were obtained with a Bomem MB-100 FTIR spectrophotometer (4 cm^{-1} resolution), using pressed ground samples with dry KBr (pellets).

Results and discussion

Structural data: XRD and FTIR

In order to analyse possible modifications in the HPW structure, X-ray diffraction and FTIR spectra were taken from samples calcined under different conditions. Powder XRD patterns indicate that the structures of samples calcined at 200 and $300\text{ }^{\circ}\text{C}$ for 2 hours are identical (Fig. 1). The positions and intensities of the main peaks ($2\theta = 10.3, 25.3$ and 34.6°) are similar to those expected for the Keggin structure.¹⁴ Also, the sample calcined at $400\text{ }^{\circ}\text{C}$ for 2 hours (Fig. 1) has almost the same d spacing, indicating the Keggin structure, but the relative intensities are different. The peaks are slightly broadened compared to those of samples treated at 200 and $300\text{ }^{\circ}\text{C}$. The sample calcined at $400\text{ }^{\circ}\text{C}$ displays a heterogeneous color on its surface, which may be indicative of partial decomposition of HPW on the surface (see below). It is known that this decomposition is affected not only by temperature but also by the time the solid is exposed to heating. Therefore, XRD of samples calcined at $300\text{ }^{\circ}\text{C}$ for 4 and 10 hours and $400\text{ }^{\circ}\text{C}$ for 4 hours were taken (Fig. 2). It is clear from the XRD pattern that the sample treated at $400\text{ }^{\circ}\text{C}$ for 4 hours underwent large decomposition forming a solid with a low degree of crystallinity containing some WO_3 phase (new broad peaks at $2\theta = 23.5, 34.6$, and 41.2°). Also, HPW calcined at $300\text{ }^{\circ}\text{C}$ for 10 hours exhibits a XRD pattern with lower intensities (Fig. 2c) compared to the sample treated for 4 hours. It should be mentioned that both samples ($300\text{ }^{\circ}\text{C}$ for 10 hours, and $400\text{ }^{\circ}\text{C}$ for 4 hours) had, at the end of calcination, a substantial portion of the solid surface colored (*i.e.* a mixture of yellow, green, and blue particles). The results demonstrate the kinetic phenomenon of decomposition of the Keggin structure, which will be discussed later.

The primary structure of HPW was examined by FTIR. Since the region between 1200 and 700 cm^{-1} is the fingerprint region for the Keggin structure, infrared spectra of samples calcined ($200, 300$, and $400\text{ }^{\circ}\text{C}$) for 2 and 4 hours (Fig. 3) were obtained. It can be observed that the characteristic bonding absorptions of the anion, P–O (1081), W=O_t (984), W–O_c–W (892 cm^{-1}), and W–O_c–W (798 cm^{-1}), are maintained for all samples, except for the sample calcined at $400\text{ }^{\circ}\text{C}$ for 4 hours. These bands are broader and of lower intensities, evidencing a relatively large amount of decomposition for the primary Keggin structure.

It has been shown in previous reports that XRD patterns of HPW differ with calcination pretreatment, due to changes in the unit cell caused by different hydration degrees. However, no mention was made as to the effects of this difference on acidity and reactivity. It is likely that a slight structural rearrangement of HPW (changed because of differences in degree of protonation) when calcined for longer periods at higher temperatures ($\geq 300\text{ }^{\circ}\text{C}$) results in solids having decreased acidities (see below). Differences in acidity are probably related to the secondary structure, since no evident

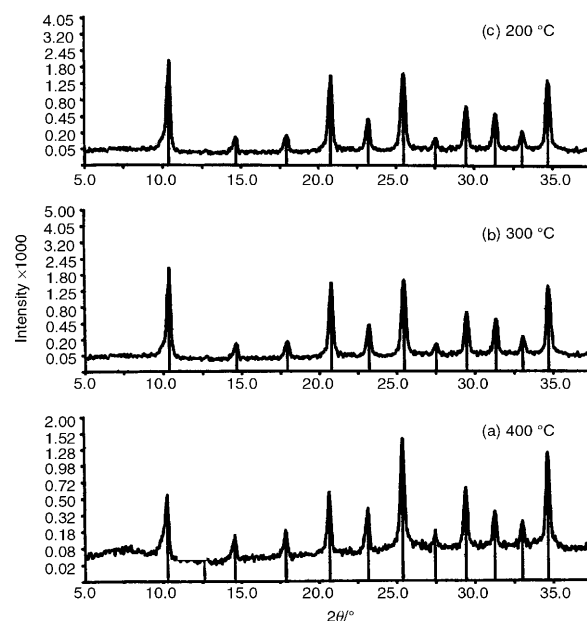


Fig. 1 XRD patterns of HPW calcined under air for 2 hours at: (a) 400 ; (b) 300 ; (c) $200\text{ }^{\circ}\text{C}$.

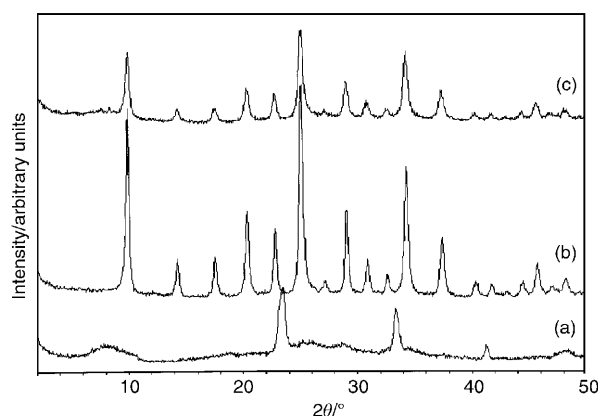


Fig. 2 XRD patterns of HPW calcined under air at: (a) 400 (4 hours); (b) 300 (4 hours); (c) $300\text{ }^{\circ}\text{C}$ (10 hours).

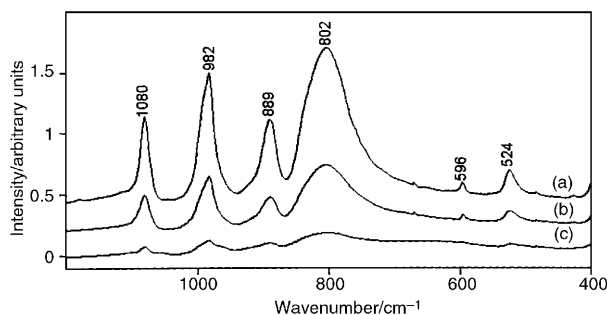


Fig. 3 FTIR spectra of HPW calcined under air at (a) 200 , (b) 300 and (c) $400\text{ }^{\circ}\text{C}$ for 4 hours. Sample pellets were 0.25% (w/w) with dry KBr.

decomposition of the primary structure was observed for short treatments at the studied temperatures.

Thermal analysis

Thermal analysis of our samples was performed to ascertain if differences in hydration could account for the discrepancies in our results from those reported previously. Thermal analysis of HPW shows three endothermic peaks in the DSC corresponding to a mass loss in the TGA. The TGA of HPW shows that mass loss occurs in three steps. The structure has been

shown to be a 24 hydrate ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 24\text{H}_2\text{O}$). Previous studies have also shown that mass loss occurs in three steps.^{11,27} The complete loss of hydration to form an anhydrous sample of HPW is a two step process. The first loss corresponds to a hexahydrate of HPW. After the second step is complete the structure is in the anhydrous form. Since our samples were calcined for 2 hours, isothermal TGA was performed at each of the various temperatures to investigate the effects of time on the thermal properties of HPW. Isothermal TGA studies for a HPW sample at 200 °C in an air flow for 2 hours demonstrate that HPW is in the anhydrous form. This is consistent with other findings when drying HPW with P_2O_5 .²⁸ Isothermal TGA analysis of samples at 300 and 400 °C gave identical thermograms confirming all samples are in the anhydrous form. Further, coupled with FTIR spectra of all samples calcined for 2 hours, it shows that no apparent decomposition of the bulk Keggin structure has occurred after thermal treatment, which had been observed previously.²⁹

Thermal decomposition of HPW

There are many complicating factors involving drying heteropoly compounds such as HPW. Generally, any polyprotic oxoacid behaving as a Brønsted acid (*i.e.* has dihydroxy functionality) can be converted into an anhydride (*i.e.* μ -oxo bridge between metals) by thermal heating. For hydrated HPW, the strongest acid is the anhydrous form, while the anhydride is weaker and formed by loss of protons connecting the Keggin units in the acid ($n\text{H}_3\text{PW}_{12}\text{O}_{40} \longrightarrow \text{PW}_{12}\text{O}_{38.5} + \frac{3}{2}n\text{H}_2\text{O}$). Thus, it is important to use the anhydrous acid in most catalytic studies involving acidity dependence.

In this study XRD, FTIR, and color change were used primarily to check decomposition of the bulk Keggin structure. Of note is the kinetic formation of the anhydride phase according to the results of XRD and FTIR for HPW calcined at different times (Figs. 2 and 3). The color change must be considered with caution. The formation of the constituent oxides of HPW (WO_3 and P_2O_5) occurs as a consequence of decomposition from the anhydride. Since this anhydride is metastable,¹⁶ only a fraction of the total calcined HPW produces WO_3 (yellow) and reduced $\text{W}_n\text{O}_{3n-1}$ (blue), which accounts for the green color observed on some samples. Changes in the color of HPW with calcination temperature have been reported before.¹¹ Although the surface of HPW is probably changed with calcination at higher temperatures, the bulk is retained as indicated by XRD and FTIR results. However, the surface amounts of the anhydride phase as well as the oxides increase with time of calcination, and are well revealed by XRD and FTIR spectra (Figs. 2 and 3). It can be concluded that this kinetic decomposition of the anhydrous HPW with consequent loss of acidity is not always sensitive to monitoring by powerful methods such as XRD or FTIR. Despite that, calorimetry is well suited to detect decomposition of anhydrous HPW. Reaction with pyridine¹⁸ or ammonia¹⁶ indicates loss of protonic acidity through the decreased heat evolved by the samples calcined at higher temperatures.

Acidity of HPW by calorimetric titration

Calorimetric results for determination of the acidic proton strength of HPW calcined at different temperatures are shown in Table 1. Titration of HPW with pyridine in a solution of CH_3CN was done three times for each sample, and the average heats used to calculate the enthalpies of interaction. It should be mentioned that the enthalpy for each sample is calculated by taking the data up to the limit of one proton equivalence ($\text{H}_3\text{PW} + \text{Py} \rightleftharpoons \text{H}_2\text{PW}^- + \text{HPy}^+$), so that the second and third deprotonation were not considered as concomitant equilibria. For the first points of titration most of the acid in solution is either totally protonated (H_3PW) or

Table 1 Thermal treatments and heat of reaction (25 ± 1 °C) of HPW with pyridine in CH_3CN solution

$T/^\circ\text{C}$, t^a/h	Total heat evolved ^b /cal	$\Delta H_{\text{lim}}^c/\text{kcal mol}^{-1}$
200, 2	5.543 ± 0.102	18.8 ± 0.2
300, 2	4.459 ± 0.107	17.5 ± 0.2
300, 10	3.832 ± 0.151	11.5 ± 0.3
400, 2	1.401 ± 0.165	8.4 ± 0.4

^a Samples of HPW treated at different temperatures and time exposed to a flow of dry air. ^b Upon complete titration of the three protons of HPW. Errors are the standard deviation of three experiments. The relatively large values reflect the cumulative process of adding heats after each addition of pyridine. ^c Calculated enthalpy obtained for the reaction of only the first proton of HPW with pyridine ($\text{H}_3\text{PW} + \text{Py} \rightleftharpoons \text{H}_2\text{PW}^- + \text{HPy}^+$). The errors are based on variance-covariance matrix analysis, but are within the estimated error of ± 0.5 kcal mol⁻¹ using the whole calorimetric curve¹⁸ (see text). Conversion: 1 kcal = 4.184 kJ.

diprotonated (H_2PW^-). Therefore, the effect of other equilibria can be simplified for calculation. It was discussed before¹⁸ that in the three step process of deprotonation of HPW in CH_3CN solution the first step is the most important to correlate with catalytic activity. The difference of this method of calculation of enthalpies for the samples in this study from the one described earlier¹⁸ (considering all three steps) is less than 0.5 kcal mol⁻¹ for the first deprotonation. From the total heat evolved in the reaction with pyridine, independently of the calculation method for the enthalpy, it is evident in Table 1 that the acid strength of samples calcined at 200 and 300 °C in air for 2 hours is superior to that of a sample calcined at 400 °C for 2 hours in air. These results are in contrast to another study in which the acidity was determined using Hammett indicators,¹⁷ but they agree well with microcalorimetric measurements of NH_3 sorption.¹⁴⁻¹⁶ It was claimed that the enhanced acidity at 400 °C was due to the HPW being anhydrous which would not be achieved by lower calcination temperatures.¹⁷ Thus, HPW was treated at 300 °C for 2 and 10 hours, and then titrated with pyridine (Table 1). It can be observed that the increased amount of time did not enhance the acidity. Actually, as stated before, the sample calcined for 10 hours showed traces of decomposition through the mixture of colors on the solid surface.

Therefore, the differences in acidity for the HPW samples must be due to other factors. First, the surface area of the solids may account for a difference in measured acidity. It is known that calcination of a solid can reduce its surface area. This is not the case in this study since the samples (200, 300, and 400 °C calcined for 2 hours) have surface areas of 6.0, 5.4, and 4.9 m² g⁻¹ respectively. In this case the surface area reduction is not very significant. Since most of the HPW protons are in the bulk of the solid (only about 0.008 mmol of protons per gram of HPW is located on the surface¹⁹ for a solid about 5 m² g⁻¹), the surface area will not bias these calorimetric results.

As mentioned earlier, heating of HPW at temperatures below its complete decomposition temperature of 500 °C might result in some reordering of the Keggin structure, or in a mass loss of the acidic protons. Reordering is not necessarily accompanied by a great mass loss. Slight rearrangement of the proton positions as well as partial decomposition forming the anhydride and/or oxide phases at higher temperatures or over longer periods probably causes the lower enthalpies calculated. To make sure that the difference in the enthalpies was not due to constraints on pyridine reacting with the protons in solution, a gas phase reaction with HPW was tested.

Dehydration of 1-propanol

It can be argued that the difference in measured acidity is due to the inability of the pyridine probe effectively to get to the

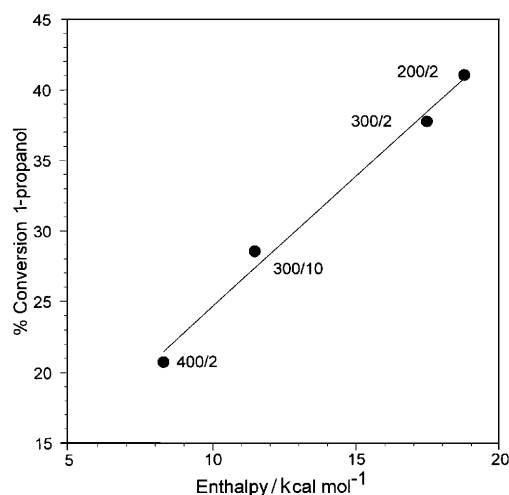


Fig. 4 Conversion of 1-propanol catalysed by HPW, calcined at different temperatures (°C)/times (h).

proton in the slightly changed HPW structure calcined at 400 °C. To investigate this possibility, samples of calcined HPW were tested for activity in 1-propanol dehydration. Since 1-propanol is a small molecule diffusional constraints due to structural rearrangements of the Keggin ion are not a factor. Fig. 4 shows the results for conversion of 1-propanol into propene at 170 °C. It is evident from these results that the activity of the sample calcined at 400 °C is inferior to that of samples calcined at 200 and 300 °C (2 and 10 hours). The acid strength, as measured by calorimetry, shows the same trend as the reaction results. Correlation of the calculated enthalpies and the percent conversion of 1-propanol is linear ($r^2 = 0.991$). Activation energies for the dehydration of 1-propanol were investigated for the calcined samples. Activation energies of 17–18 kcal mol⁻¹ were found for the samples calcined at 200, 300 and 400 °C. These results are in the range for other solid acids used for dehydration of 1-propanol,³⁰ and are consistent with no diffusional constraints.

Conclusion

It has been shown that calcination treatment has a profound effect on the acidity of HPW. Samples calcined in air at 200, 300 and 400 °C for two hours are all in the anhydrous form of HPW. No evident decomposition of the bulk Keggin structure was observed, although the sample calcined at 400 °C showed color modifications on its surface. Longer treatments at temperatures higher than 300 °C clearly indicated changes of its primary structure. Samples of HPW calcined, for the same amount of time, at 200 and 300 °C have higher acidities and reactivities than a sample calcined at 400 °C. The difference is

probably due to a slight structural rearrangement of HPW and/or a small amount of decomposition of the anhydrous HPW forming the anhydride phase. This results in a solid of lower acidity. The acidity of HPW calcined at different temperatures has been measured by solution calorimetry, and correlated to the dehydration of 1-propanol as a model reaction. The coupled methods can be used to monitor loss of acidity by HPW after thermal treatments.

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