Synthesis, characterization & reactions of vanadium substituted 12-molybdo heteropoly acids†

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12-Phosphomolybdic acid and its mono-, di-, and tri-substituted vanadium analogues have been synthesized and characterized by instrumental techniques. The catalytic activity of these compounds has been studied and compared for the oxidation of cyclohexanol to cyclohexanone using hydrogen peroxide as the co-oxidant. It has been found that at low concentrations of hydrogen peroxide the catalytic activity is lowered as the number of vanadium atoms is increased, but when excess of hydrogen peroxide is used the catalytic activity is found to follow the reverse trend. The results are explainable in terms of the V⁴⁺ content in the compounds.

Heteropoly acids (HPA) are well known active catalysts for various catalytic reactions due to their acidic and redox properties. The 12-phosphomolybdic acid, and particularly its derivatives containing vanadium, have been used in both homogeneous and heterogeneous oxygenation and oxydehydrogenation type of reactions. Catalytic reactions involving both unsupported and supported HPA catalysts have been tried out in the past. In the vanadium substituted HPA, H₃₋ₓPMO₁₂₋ₓVₓO₄ₓ (n = 0, 1, 2, 3), the number of acidic sites increases as n is increased due to the substitution of hexavalent Mo by pentavalent V atoms. Heteropoly acids have fairly good thermal stability, and by using potassium salts of the heteropoly acids or silica as a support, their thermal stability can be increased considerably. 12-Phosphomolybdic acid and its vanadium substituted analogues are increasingly being used as active catalysts for selective oxidation of organic compounds. The acidic and redox properties of the catalyst depend on the degree of vanadium substitution and the redox route is proposed as a more favoured one than the acid route when the degree of vanadium substitution is increased. However, the effect of vanadium substitution is reported to show opposite effects. Introduction of vanadium lowers the catalytic activity of the unsupported acids where as the supported samples become more active with the degree of vanadium substitution.

Various studies on the characterization and catalytic activities of the unsubstituted and the vanadium substituted phosphomolybdic acids have been performed in the past. It has been reported that among the various vanadium substituted compositions, the divanado-compound shows the maximum catalytic activity. Because of the higher redox potential of vanadium compared to that of molybdenum, the vanadium substituted compounds are expected to be more active in redox type catalytic reactions. Thus one expects an increased activity with increased vanadium substitution, even on unsupported catalysts. Even though a number of studies have been performed on various catalytic reactions involving these compounds, there has been no systematic study to probe the unexpected decrease in the catalytic activity of the unsupported vanadium substituted HPAs. We have studied this in detail after systematic characterization of the catalysts. The oxydehydrogenation reaction of cyclohexanol to cyclohexanone is probed using the n = 0-3 HPA as homogeneous catalysts using hydrogen peroxide as the oxidant.

Materials and Methods
The dodecamolybdate, H₃PMO₁₂O₄₀xH₂O (V₀), was a reagent of Loba Chemie, GR grade. The vanadium substituted compounds H₃₋ₓPVₓMo₁₂₋ₓO₄ₓ.xH₂O (n = 1,2,3) were prepared according to the method of Tsigdinos and Hallada and purified by repeated crystallization from water. The exact degree of hydration of the crystalline hydrates was determined by thermogravimetric analysis. Cyclohexanol and H₂O₂ (15% solution) were reagents of Loba Chemie (GR grade).

The catalytic reactions were carried out in a round bottom flask (50 ml) provided with a double walled condenser. In a typical reaction, the catalyst (100 mg) was added to cyclohexanol (3 g; 0.03 mol), varying amounts (0.013 - 0.0405 mol, in steps of 0.0045 mol) of hydrogen peroxide were added and the contents refluxed for 3 hr with stirring. The reactions were carried out at different temperatures (30-80°C) in an oil bath. The reaction product was isolated and analyzed on a Shimadzu gas
chromatograph provided with TCD detector and Carbowax 1560 column. Percentage conversion of cyclohexanol to cyclohexanone was calculated by area normalization techniques.

Thermogravimetric analyses were carried out on a Seiko Instruments TG/DTA 32 thermal analyser in static air at a heating rate of 10°/min. Approximately 10 mg of sample was used each time. Powder XRD patterns of the HPA were recorded on a Rigaku D-Max diffractometer using Cu-Kα radiation. EPR spectra were recorded at room temperature using a Bruker ER2000 X-band EPR spectrometer. Infrared spectra were recorded in nujol mull with a Perkin-Elmer 1620 FT-IR spectrophotometer. UV-visible spectra were obtained using a Shimadzu UV 210IPC UV-Vis scanning spectrophotometer. Spectra were recorded using a 5 mmol water solution of the compounds.

Results and Discussion
1 Catalyst characterization
(A) Thermal analysis
The unsubstituted and the vanadium substituted heteropoly compounds were initially characterized by thermal analysis methods. The degree of hydration of the HPAs was determined from TGA analysis. The unsubstituted and the three vanadium substituted compounds corresponded to the formulae $H_{12}PMo_{12}O_{40} \cdot 15H_2O$, $H_5PMo_{11}VO_{40} \cdot 29H_2O$, $H_5PMo_{10}V_2O_{40} \cdot 27H_2O$ and $H_5PMo_9V_3O_{40} \cdot 18H_2O$ respectively (Table 1), hereafter referred to as V-0, V-1, V-2 and V-3 respectively.

TG, DTA and DTG curves of the four heteropoly compounds are shown in Fig. 1. It may be seen that all the four TG curves show some common features. Below 200° four distinct mass loss regions can be seen in DTG curves, and the corresponding DTA curves also show endothermic peaks. These endothermic DTA peaks are due to loss of water molecules from the samples which are associated with mass loss in the corresponding TG curves. The first two mass loss regions are not clearly separated in the TGA curves. The first two and the last two mass loss regions are separated by a small flat region. The overall mass loss and the number of water molecules lost at each mass loss step below 200° are given in Table 1. In all the four compounds the last two mass losses which occur above 90° correspond to nine water molecules, and in this region the two mass loss steps at 100° and 115° correspond to 4 and 5 water molecules respectively. The first two mass losses below 90° vary from compound to compound and no typical trend is observed.

![Fig. 1 - TG-DTG-DTA curves of 12-phosphomolybdic acid and its three vanadium substituted compounds: (a) unsubstituted acid (V-0); (b) mono- (V-1); (c) di- (V-2) and (d) tri- (V-3) vanadium substituted analogues.](image-url)
Table 1 — TG-DTG-DTA results of 12-phosphomolybdic acid and its vanadium substituted compounds

<table>
<thead>
<tr>
<th>Sample</th>
<th>TG/DTA peak temp., °C</th>
<th>No. of H₂O lost</th>
<th>Water of hydration</th>
<th>Water of crystallization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt; 90°C</td>
<td>&gt; 90°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V-0</td>
<td>40.65</td>
<td>100.115</td>
<td>6 (2+4)</td>
<td>9 (4+5)</td>
</tr>
<tr>
<td>V-1</td>
<td>60.75</td>
<td>100.115</td>
<td>20 (16+4)</td>
<td>9 (14+5)</td>
</tr>
<tr>
<td>V-2</td>
<td>60.75</td>
<td>100.115</td>
<td>18 (14+4)</td>
<td>9 (14+5)</td>
</tr>
<tr>
<td>V-3</td>
<td>50.70</td>
<td>100.115</td>
<td>9 (5+4)</td>
<td>9 (4+5)</td>
</tr>
</tbody>
</table>

The mass loss in the first part which occurs below 90° is almost continuous from room temperature to 80°. However, DTG and DTA curves show that water loss occurs in two steps in this temperature region. For V-0, two distinct steps are clearly seen in the TGA curve and for the other samples this step-wise water loss is not clear. Rough calculation (based on the mass loss at the temperature between the first two DTG or DTA peaks) shows that the second mass loss step in the first part (i.e., below 90°) corresponds approximately to four water molecules. Only the initial mass loss which starts just above the room temperature up to 60° (DTG peak position) varies with composition and this is due to loosely bound water molecules which are prone to easy dehydration. It has already been reported that the degree of hydration in these heteropoly compounds depends on various factors such as relative humidity, degree of drying, solution acidity, temperature etc.²⁰⁻³

The number of water molecules lost above 60° in the three steps adds up to 13 and this explains the unusual stability²⁴ of the unsubstituted or vanadium substituted HPAs with degree of hydration equal to 13. This also predicts that degree of hydration of 9 or 5 is also possible for the HPAs. The HPAs with high degree of hydration of 30 or above, on evacuation or keeping in air, lose hydrated water and a minimum of 13 H₂O is reported for these compounds.²⁵ However, the corresponding tungsten analogues are reported²⁶ to be stable with degree of hydration of 5 or 9. From Table 1 it may be concluded that the water losses occurring at ~70°, 100° and 115° are not affected by vanadium substitution and these water molecules are strongly coordinated to the Keggin structure.

Even though the first four mass losses occur at almost the same temperature in all four compounds, there is a marked difference in the temperature at which constitutional water is lost. This occurs in the temperature region 400-450° for the unsubstituted compound, and the corresponding temperature at which this loss occurs decreases with the number of vanadium substitutions. Thus for V-1 this temperature range is 300-350°, for V-2 250-300° and for V-3 it is in the range 200-250°. From these results it may be concluded that as the number of vanadium substitutions increases, the thermal stability of the heteropoly compounds decreases considerably.

(B) X-ray diffraction studies

The formation of the vanadium substituted heteropoly acids is confirmed by powder X-ray diffraction. The XRD pattern of V-1 was identical to that of the unsubstituted HPA having a cubic structure with the lattice parameter a = 23.25 Å. The XRD pattern of V-2 could be indexed on a tetragonal cell with lattice parameters a = 12.9 Å and c = 18.3 Å. These values are close to that reported earlier²⁷ for the same compound with degree of hydration equal to 30. The XRD pattern of V-3 is closely related to that of V-2 but a few weak additional reflections were observed apart from those arising from a reported unit cell dimension of a tetragonal cell.²⁸ The extra weak reflections could be due to the fact that there is a large decrease in the degree of hydration (18 H₂O instead of 30 H₂O for which the crystal structure is reported) for which a low symmetric structure is expected. HPAs are known to show different crystal structures depending on the degree of hydration. For example, the unsubstituted HPA, H₃PMo₁₂O₄₀ is reported to have a cubic²⁷, tetragonal²⁹ or triclinic³⁰ geometry with various amounts of water of hydration.

(C) EPR studies

EPR spectra of the vanadium substituted heteropoly acids show that the compounds contain small amounts of vanadium as V⁴⁺. In fact, the spectra resemble those of other V⁴⁺ containing compounds. A typical spectrum of the V-2 compound is shown in Fig. 2. The EPR spectra of the compounds are identical to those reported earlier by various groups²¹⁻²³. A complex pattern with many lines is obtained due to the hyperfine splitting of the I = 7/2 V⁴⁺.
centres (8 lines are expected). The parallel and perpendicular components are not completely resolved which may be due to broadening of some of the features. Some of the components are clearly seen separately with $A_1 = 200$ G and $A_2 = 75$ G and most other splittings correspond to the isotropic value $A_{iso} = 100$ G ($A_{iso} = 1/3 A_1 + 2/3 A_2$).

Double integration of the EPR spectra of V-1, V-2 and V-3 gave the approximate concentration of $V^{4+}$ in these compounds. The calculated values correspond to 4.3%, 8.9% and 13.8% respectively for the mono-, di- and tri-substituted compounds respectively. These values are almost in the ratio 1:2:3, which indicates that substitution by each vanadium gives rise to approximately 4.5% $V^{4+}$ in these compounds. Since molybdenum is present in its highest oxidation state in these compounds, it is possible that $V^{4+}$ centers are formed either during the synthesis of the compounds due to the presence of small amounts of reducing substances in the starting materials or due to reduction of some vanadium during the processing of the samples. The latter seems to be more reasonable as it was found that the amount of $V^{4+}$ in the compounds increased considerably with time as evidenced by the enhanced EPR signal intensity.

(D) Infrared spectra

The infrared spectra of the phosphomolybdic acid and its mono-, di- and tri- vanadium substituted analogues exhibit bands in the range 3200-3600 cm$^{-1}$ and 1600-1700 cm$^{-1}$ due to $v$(O-H) and $v$(H-O-H) respectively for water of crystallization and constitutional water present in the HPA.$^{13,15,39}$ Apart from these bands, the unsubstituted HPA shows four major peaks at 1064, 960, 868 and 790 cm$^{-1}$ due to $v$(P-O$_a$), $v$(Mo=O)$_b$, $v$(Mo=O$_c$-Mo) and $v$(Mo=O$_d$-Mo) respectively where the subscripts $a$, $b$, $c$ and $d$ indicate different types of O in the Keggin Unit. These bands are shifted to lower frequency region in the vanadium-containing derivatives due to the weakening of P-O and Mo-O bonds and also may be due to the increase in the number of protons from 3 to 6 (as the number of vanadium atoms are increased from 0 to 3).

(E) Electronic spectra

Electronic spectra in the UV region of all the four compounds (V-0, V-1, V-2 and V-3) show an intense band at 220 nm whose intensity decreases and the band becomes broader as the number of substituted vanadium is increased. Apart from this intense band at 220 nm, a broad, weak band appears at 310 nm in the vanadium substituted compounds which is observed as a weak shoulder in the unsubstituted compound. The spectra of the four compounds under investigation are shown in Fig. 3 in the wavelength region 260-540 nm.

Neumann et al.$^{40}$ have reported two main UV bands at 220 nm and 310 nm in the spectrum of the di-vanado substituted phosphomolybdic acid, recorded under various experimental conditions. Centi et al.$^{34}$ have also reported that the weak and broad band at 310 nm in the spectrum of the unsubstituted compound is due to lowest energy charge transfer band of Mo-O in octahedral coordination. Our results give further evidence for this assignment. The intensity of the absorption band at 220 nm decreases as the degree of vanadium substitution increases through which the overall molybdenum concentration is decreased from 12 (for V-0) to 9 (for V-3). Additional evidence for such a conclusion comes from the calculated area under the curve for the band at 310 nm. For the vanadium substituted compounds, areas under the curves are calculated after drawing an exponential base line (shown in Fig. 3). The computed areas are in the ratio 1:0.92:0.81 for V-1, V-2 and V-3 respectively and when this value is normalized for 11 molybdenum atoms for V-1, the calculated values are found to be in the ratio 11:10:9 which exactly is the number of molybdenum atoms in the vanadium substituted compounds. Thus the optical spectra of the phosphomolybdic acids in the ultraviolet region can be used as a tool for quantitative estimation of the degree of substitution in the primary site.

2 Catalytic reactions

Oxidation of the secondary alcohol cyclohexanol to cyclohexanone has been carried out to study the catalytic activity of the vanadium substituted phosphomolybdic acids. The reaction has been carried out at different temperatures and with different mole proportions of hydrogen peroxide by varying the amount of the catalyst. There was not much variation in the catalytic activity with the amount of the catalyst. The same trend was observed at different temperatures. Similarly, initial studies showed that maximum conversion was observed when the reaction was carried out at 65°. Thus the catalytic reactions were studied using 100 mg of the catalyst sample at a fixed temperature (65°).
The percentage conversion of cyclohexanol to cyclohexanone is shown in Fig. 4 for the unsubstituted phosphomolybdic acid and the three different vanadium substituted compounds as a function of the amount of hydrogen peroxide used. The result obtained in the absence of the catalyst, under the same conditions, is also presented for comparison. The conversion was very low when no catalyst was used. For the unsubstituted catalyst, the conversion is better than that in the absence of the catalyst but is also independent of the amount of hydrogen peroxide. However, an interesting behaviour is observed when the vanadium substituted compounds are used as catalysts. Initially for the same amount of hydrogen peroxide, the catalytic activity of V-1 is better than that of V-0, whereas for V-2 and V-3 the activity is found to be considerably decreased compared to that for V-1. Thus initially V-1 shows maximum catalytic activity which decreases as the degree of vanadium substitution is increased from 1 to 3. In fact the initial degree of conversion is less for V-3 than that of the unsubstituted catalyst (V-0).

However, the catalytic conversion curves show interesting behaviour when the amount of hydrogen peroxide is increased further. The percentage conversion of cyclohexanol to cyclohexanone increases for all the three vanadium substituted HPA catalysts as the amount of the oxidant is increased as may be seen in Fig. 4. Thus for V-1, a maximum conversion of 9% is observed when 0.025 mol of hydrogen peroxide is used whereas for V-2 and V-3 the amount of hydrogen peroxide required for maximum conversion is 0.03 and 0.035 mol respectively. The maximum percentage conversion using V-2 and V-3 with these amounts of hydrogen peroxide is found to be 10% and 12% respectively. Addition of large excess of hydrogen peroxide has no effect on the activity of the catalysts, the conversion remains almost constant at higher concentrations of the oxidizer, as may be seen in Fig. 4. This is found to be true for all the three vanadium substituted HPAs. Thus it is observed that at very low concentration of the oxidizer, the mono-vanadium substituted catalyst shows maximum conversion for the oxidation of cyclohexanol to cyclohexanone and the catalytic activity decreases with further substitution of vanadium for molybdenum in the HPA. At higher concentrations of the oxidizer, the catalytic activity of the vanadium substituted compounds shows a reverse trend, the catalytic activity increases with degree of vanadium substitution.

From the results it is clear that the catalytic oxidation of cyclohexanol to cyclohexanone can be accelerated if the degree of vanadium substitution of the HPA catalyst is increased. Among the four compounds V-3 emerges as a promising candidate for the catalytic oxidation. The above results may be explained in the light of the results from the EPR studies.

It has been observed that as the number of substituted vanadium atoms is increased from 1 to 3, there is a corresponding increase in the amount of V$^{5+}$ in the compounds. Part of the hydrogen peroxide added is used for the conversion of the reduced vanadium centers to V$^{5+}$ and only the remaining hydrogen peroxide is available for oxidation purposes. Thus, more hydrogen peroxide is required to obtain maximum conversion as the number of substituted vanadium is increased in the catalysts. At low concentrations of the oxidizer, most of the hydrogen peroxide is used for the oxidation of vanadium and thus the degree of conversion decrease in the order V$^+_{1} > V^+_{2} > V^+_{3}$. The reverse trend is observed at higher concentrations of hydrogen peroxide. This result points to the fact that vanadium in +5 oxidation state is the catalytically active center and vanadium centers are more active than the corresponding molybdenum centers.

The fact that there is initial oxidation of V$^{4+}$ to V$^{5+}$ is further confirmed by EPR analysis. For this purpose the vanadium containing catalyst was initially refluxed with hydrogen peroxide for a long time and the EPR spectrum of the recovered compound was recorded. EPR spectrum of this pre-oxidized catalyst is shown in Fig. 2b. It may be seen that there is a considerable decrease in the intensity of the EPR signal compared to that of the non-oxidized catalyst. Catalytic activity of the oxidized V-2 sample was tested in a similar fashion as in the previous cases and it was observed that maximum conversion was obtained with less amounts of the oxidizing agent. However, it was not possible to convert V$^{4+}$ to V$^{5+}$ completely by this pre-oxidation process.

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