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Abstract

Recent studies of the synthesis of V_2O_5 gels by acidifying metavanadate salt solutions suggest that dioxovanadium cations polymerize into chains of vanadate octahedra. In this study we characterize the growth of vanadate polymers by both solution and MAS ^{17}O NMR. The spectra are consistent with the formation of a chain polymer with a repeat unit of $V_{Oh}O_2(OH)(OH_2)_2$. The ^{17}O NMR spectra also suggest that the chains might connect to each other through hydrogen bonding.

Key words: ^{17}O NMR, V_2O_5 gels, MAS NMR

Introduction

Though the chemistry of V_2O_5 gels has been of recent interest[1-11], the reason that the acidification of vanadate solutions produces a characteristic 2-D ribbon microstructure[1,2,5,6] remains unclear. Previous workers have proposed that a two-dimensional fragment of vanadium pentoxide crystal is formed[8,9], but recent work using EPR and ^{51}V NMR has instead suggested the chain polymerization of the dioxovanadium cation[7].

In this work, we investigate whether ^{17}O NMR spectra are consistent with the chain growth mechanism by labelling the vanadate solution species and intermediate polymers with ^{17}O early in the synthesis. Using ^{17}O NMR chemical shift assignments from several studies of vanadate structures in solution[12-20], we are also able to speculate as to whether hydrogen bonding occurs among the polymer chains in a way that might serve to build 2-D structures recently observed by cryo-TEM[10,11].

Experimental

Samples were prepared by dissolving sodium metavanadate in 1 gram of 10 atom% ^{17}O enriched water (Aldrich Chemical). One further gram of unenriched water was then added to yield a stable 1.0 M sodium metavanadate solution (pH=8). Adding the ^{17}O enriched water first served to increase the extent of ^{17}O enrichment into the vanadate species over the time period studied. A column of Dowex 50W X-2 50-100 mesh ion exchange beads was charged with hydrochloric acid, was washed with deionized/distilled water, and was then used to acidify the solutions.

NMR spectra were acquired on a GE 500 MHz NMR spectrometer. ^{51}V NMR solution spectra were acquired at 131.487 MHz using a 90° pulse width of 12 μs, a spectral width of 60 kHz, a relaxation delay of 0.5 s, and with 256 transients. ^{17}O NMR solution spectra were acquired at 67.8087 MHz using a 90° pulse width of 61 μs, a spectral width of 111 kHz, a relaxation delay of 0.1-0.2 s, and with 10,000 transients. ^{51}V and ^{17}O chemical

shifts were calculated with reference to external samples of vanadium oxy-trichloride ($VOCl_3$) and water, respectively.

Magic angle spinning (MAS) spectra were acquired with a 5 mm Doty probe at a spinning speed of 10 kHz using Si_3N_4 sample rotors. Prior to spectral acquisition, excess solution was removed from the gelled sample by filtration to maximize the proportion of ^{17}O enriched gel in the solid and to remove any dissolved species still present. Spectrometer parameters were the same as for solution spectra except that 1,000 and 50,000 transients were used for ^{51}V and ^{17}O MAS NMR, respectively.

Results and Discussion

The ^{51}V NMR spectrum of the sol immediately after ion-exchange is shown in Figure 1. Detailed discussion of the assignments can be found in reference 7. The peaks at -426, -513, and -532 ppm correspond to the fast proton exchange limit of the di- and tri- protonated forms of the decavanadate anion, and the peak at -545 ppm corresponds to the dioxovanadium cation[7]. The remaining peaks at -523 and -537 ppm are assigned to the triprotonated form of the decavanadate anion[7,21,22]. The progression of the ^{51}V NMR spectra as gelation occurs has been presented and discussed in reference 7.

^{17}O NMR is used here only to identify the intermediate and final structures of the V_2O_5 gel. Due to the low enrichment and unknown isotope exchange rate used, a kinetic analysis is not expected, and such an analysis has already been performed using ^{51}V NMR and Electron Paramagnetic Resonance (EPR)[7].

The ^{17}O NMR spectrum immediately after ion-exchange is shown in Figure 2, and the progression of the ^{17}O NMR spectra as gelation occurs is shown in Figure 3. The peaks at 80 ppm ($V_6\underline{O}$); 348 ppm ($V_3\underline{O}$); 705, 843, 931 ppm ($V_2\underline{O}$); and 1199, 1210 ppm ($V\underline{O}$) have all been assigned previously to the indicated oxygen sites in the decavanadate species at pH=2[12,13,14,15]. These peaks each represent both protonated and deprotonated forms of the decavanadate anion undergoing fast exchange. This fast

exchange limit can depend on the solvent and solution concentration[24]. At this high concentration, apparently some decavanadate anion can be formed that does not exchange quickly enough to cause peak coalescence[7]. Hence, the ^{17}O NMR peak at 453 ppm matches a peak observed for an $H_3V_{10}O_{28}^{3-}$ oxygen site undergoing slow exchange[14]. It is assigned to the triprotonated decavanadate anion since this peak is present throughout gelation in a fashion micmicking the corresponding ^{51}V NMR peaks at -523 and -537 ppm[7,21,22]. The appearance of the triprotonated form of the decavanadate anion suggests that the decomposition of the decavanadate anion into the dioxovanadium cation might involve the protonation of the diprotonated decavanadate anion (decavanadic acid)[7]; e.g.,

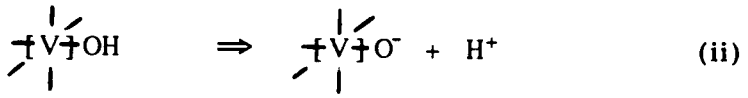
$$H_2V_{10}O_{28}^{4-} \xrightarrow{H^+} H_3V_{10}O_{28}^{3-} \xrightarrow{13\ H^+} 10VO_2^+ + 8\ H_2O \qquad \text{(i)}$$

In this study, the triprotonated decavanadate anion is present for somewhat longer periods of time (Figure 3) than at the lower concentration sols studied previously[7].

Having accounted for all possible ^{17}O decavanadate peaks, we then associate the small ^{17}O peaks observed at 220, 580, 1050 and 1380 ppm with non-decavanadate species. The peak at 220 ppm is present throughout gelation. To assign this peak, we compare it with the spectrum of a vanadate solution containing a high concentration of dioxovanadium cation as demonstrated by the ^{51}V spectrum (Figure 4). The ^{17}O NMR spectrum of the dioxovanadium cation solution in Figure 4 shows the same peak at 220 ppm. Since, according to Howarth and coworkers, the V=O bond of the dioxovanadium cation is not observable in aqueous solution[17,18], we propose to assign this peak to water molecules that are coordinated to the vanadium. This is a triply coordinated oxygen site ($V\text{-}OH_2$), so it is reasonable that it should be near the peaks of the V_3O groups of the decavanadate anion[12,13,14,15]. This assignment is also consistent with the chemical shift of the

coordinated water in $V^{IV}O(H_2\underline{O})_5^{2+}$, which appears at ~180 ppm in aqueous vanadyl sulfate solutions[25].

The ^{17}O NMR peaks at 580, 1050, and 1380 ppm clearly disappear from the solution spectra after the initial polymer growth occurs[7]. Previously reported ^{51}V NMR solution spectra[7] and the ^{17}O NMR spectra (Figures 2 and 3) show that no new mobile vanadate species are formed in solution during gelation[7], so we deduce that these three ^{17}O peaks are associated with the growing vanadate polymer whereas the corresponding ^{51}V polymer peaks were not well resolved[7]. These three ^{17}O peaks are well resolved, perhaps because the anisotropy of the ^{17}O sites in the polymer is less severe than of the ^{51}V sites. The 580 ppm peak is near $V_2\underline{O}$ peaks from decavanadates[12,13,14], and chemical shift correlations of $V_2\underline{O}$ bond angles in aqueous salt solutions containing dimers and cyclic species show that it might correspond to a $V_2\underline{O}$ bridge at ~160-180°[15,16,18]. ^{17}O NMR studies of vanadate peroxy compounds and of the decavanadate anion suggest that the peak at 1050 ppm corresponds to a terminal V-$\underline{O}$ group[12-16]. This peak probably shows the exchange-averaged shift for a V-$\underline{O}$H site on the polymer undergoing the fast reaction[19];



(ii)

The 1380 ppm peak may be associated with the V=$\underline{O}$ group on the vanadate polymer. Though the V=$\underline{O}$ site can not be observed for the dioxovanadium cation[17,18], ^{17}O NMR studies on $VO(NO_3)_3$ and $VOCl_3$ show that short V=$\underline{O}$ bonds have a chemical shift of ~1400 ppm.

The suggestion from our previous ^{51}V NMR kinetic study that the polymer is built by chain polymerization of the dioxovanadium cation[7,26] is supported by the appearance of the linear oxygen bridge at 580 ppm in the ^{17}O NMR solution spectra. Further evidence is obtained by examining the gel with MAS NMR. The ^{51}V MAS NMR spectrum of the

undried gel (Figure 5) shows only one peak at -547 ppm. This is consistent with spectra reported earlier and corresponds to an octahedral environment[7,27,28]. All peaks observed in the corresponding ^{17}O MAS NMR spectrum (Figure 6) should be associated with this sole ^{51}V environment. The ^{17}O MAS NMR of the wet gel shows peaks at 223, 688, 1150, 1380, 1396, 1407, and 1430 ppm. The peak at 223 ppm is associated with coordinated water molecules as above. The peak at 688 ppm is near the chemical shift range of $V_2\underline{O}$ environments for decavanadates[12-15]. The peak at 1150 ppm is near that for terminal $V\underline{O}$ sites in decavanadates[12,13,14,15,16]. The peaks at 1380, 1396, 1407 and 1430 ppm are all consistent with $V=\underline{O}$ bonds[17]; the formation of multiple peaks (cf. the single solution ^{17}O NMR peak observed at 1380 ppm in Figure 2) may result from different degrees of hydrogen bonding in the same way that ^{17}O chemical shifts are affected by hydrogen bonding between water and $C=\underline{O}$ groups[29,30,31].

These peak assignments suggest what the repeat unit of the polymer might be. Since microscopic observations show linear polymer growth, the two bridging oxygens should be on opposite sides of the vanadium center[10,11]. Moreover, EPR, IR and Raman studies show that one of the two water molecules is opposite the $V=\underline{O}$ bond[3,32,33,34]. A possible structure is shown in Figure 7. There are no reports of optical isomerism, so the equatorially coordinated water and hydroxyl groups can presumably switch positions on the vanadium center. We note though that while the expected ratio of these oxygen sites from Figure 7 is $O_{br} : O_t : OH : OH_2 = 1 : 1 : 1 : 2$, the ratio of the ^{17}O peak intensities is approximately 1 : 1 : 0.5 : 1. This discrepancy might be due to the exchange of ^{17}O isotope between the enriched $-\underline{O}H_2$ sites and the less enriched bulk water. This process has been confirmed and studied in vanadyl sulfate solutions[25].

Although there is a possibility of short-lived and/or low concentration intermediates that are undetectable by NMR occurring in the polymerization process, the similarity of the repeat unit in Figure 7 to the structure of the dioxovanadium cation suggests that the polymerization process might require no other intermediates. The

hydroxyl group on the repeat unit could be the result from hydrolysis of a coordinated water on the just-polymerized dioxovanadium cation[7].

Hydrogen bonding between these chains[30] is hinted at by the downfield shift of the $V_2\underline{O}$ and $V\underline{O}H$ peaks of the polymer compared to the signals of these sites in solution. Since no dissociation of the polymer formed is observed by either ^{17}O or ^{51}V NMR during gelation[7], the most likely explanation for the disappearance of the solution ^{17}O NMR peaks at 580 and 1050 ppm is the broadening caused by continued polymer growth and hydrogen bonding. This might also account for the reappearance of these peaks (shifted to 688 and 1150 ppm) in the ^{17}O MAS NMR. A hypothetical structure is shown schematically in Figure 8 and is consistent with the electron diffraction pattern from cryo-TEM studies on the wet gel[10,11]. Note that since the ^{17}O peak of the coordinated water shows no downfield shift, it might not interact with any hydroxyls.

Previous cryo-TEM observations have shown that the gel ribbons are ~25 nm in width, so the transverse assembly of linear polymers shown in Figure 8 must cease at some point else sheets would be produced. This cessation may be caused by the presence of negatively charged ligands in the equatorial position in Figure 7.

The reaction mixture remains at a constant pH of 2, and since neither mobile vanadate anions nor counterions (e.g. Cl^-) are present in the sols at this concentration, only the linear vanadate polymers can provide such buffering capacity. These negative charges could only be the result of further deprotonation of the hydroxyl group on the repeat unit.

$$VO_2(OH_2)_2(OH) \quad \Rightarrow \quad VO_2(OH_2)_2O^- + H^+ \qquad \text{(iii)}$$

We might not expect to see the O^- site in the ^{17}O NMR spectra because of its low concentration and fast exchange.

At the concentration where the ribbons were observed with cryo-TEM (0.5M vanadate), one of every 50 vanadia repeat units should be negatively charged to maintain the pH. If this change were responsible for halting the ribbon's transverse growth (by interfering with the hydrogen-bonding mechanism), then using bond lengths cited in references 25,35, and 36, and the hypothetical configuration shown in Figure 8 we might expect the width of a 50 chain ribbon to be in good agreement with that observed with cryo-TEM (~25 nm)[11].

The ribbon structure shown in Figure 8 should be stable upon drying at room temperature since XRD, IR, and Raman studies have indicated the short V=O bond and the coordinated water opposite it are retained even after drying[1,32,33,34,37]. The same characteristic ribbon structure and electron diffraction pattern are also retained[5,6]. IR and NMR studies have shown that the V-OH groups are largely retained upon drying, so apparently there are no condensation reactions between V-OH groups[32,38,39,40]. If the linear bridges between vanadia octahedra remain unchanged[41,42,43,44], the only change in structure we might expect with drying would be the loss of the equatorial coordinated water to allow association with the oxygen of the V-O-V bridge of an adjacent chain. This would suggest the structure shown schematically in Figure 9 with the formula, $V_2O_5 \cdot 3H_2O$. We note, though, that this indicates somewhat more water than the usual hydrated gel formula of $V_2O_5 \cdot 1.6H_2O$ obtained from thermogravimetric (TGA) analysis[1,33].

Conclusions

^{17}O NMR spectra are consistent with two earlier points suggested by ^{51}V NMR: 1) that the dioxovanadium cation forms a chain polymer and 2) this polymer can undergo hydrolysis to form V-OH sites [7]. Evidence from ^{17}O NMR also suggests that the hydrolyzed, linear polymers may assemble into a ribbon structure by aligning hydroxyl

groups, bridging oxygens and equatorially coordinated waters to achieve hydrogen bonding.

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Figure 1. ^{51}V Solution NMR Spectrum of Reacting Solution (t=0)

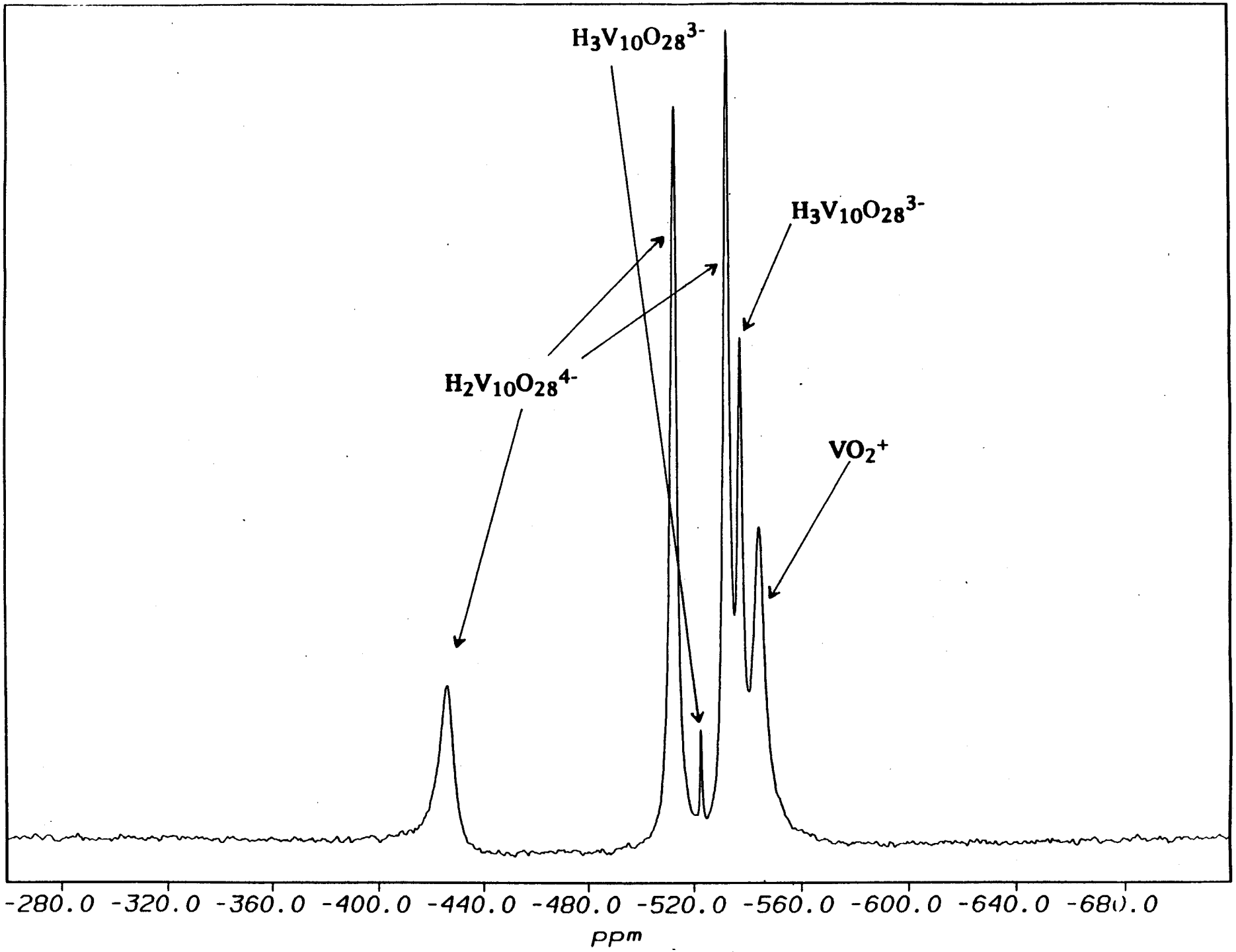


Figure 2. ^{17}O Solution NMR Spectrum of Reacting Solution (t=0)

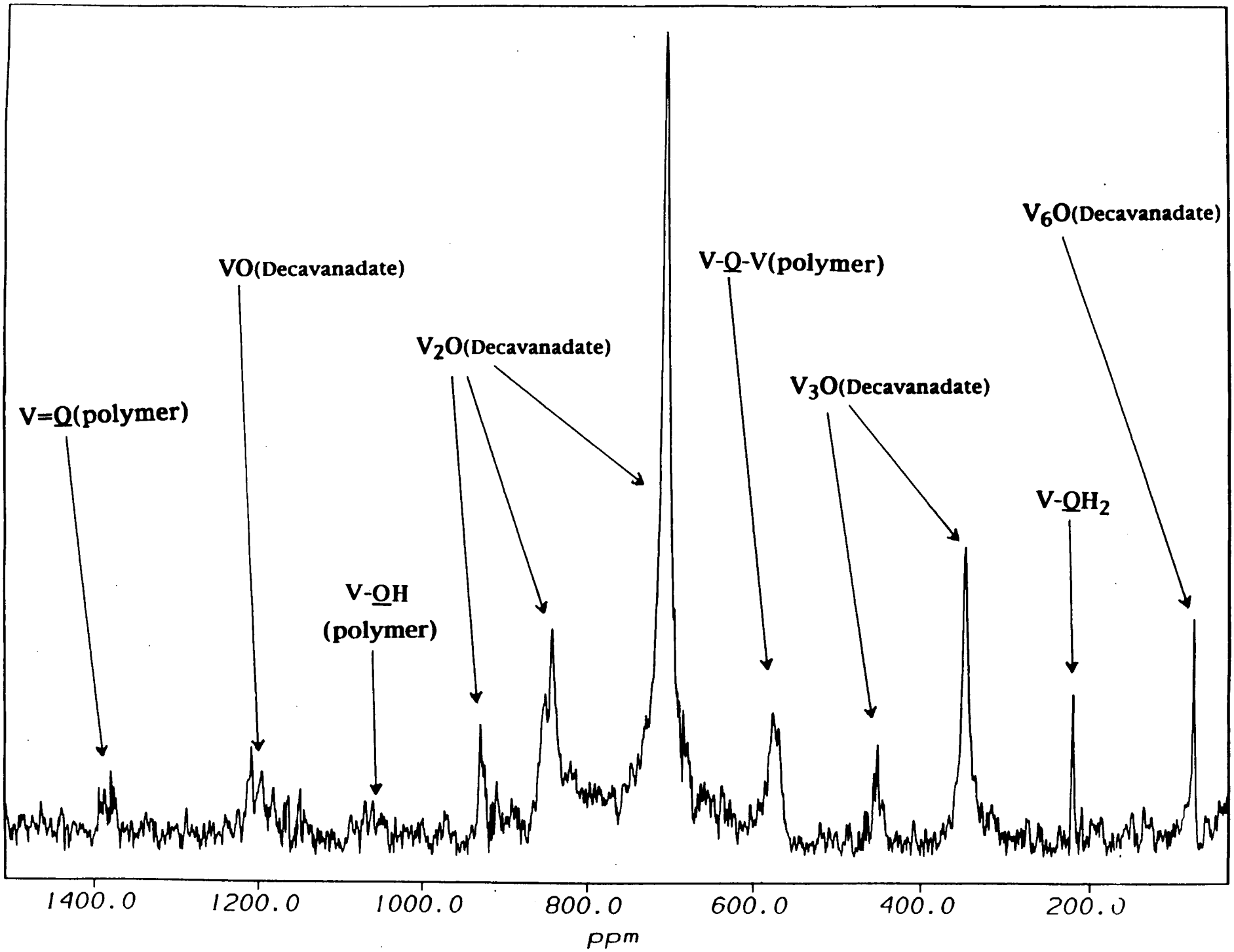
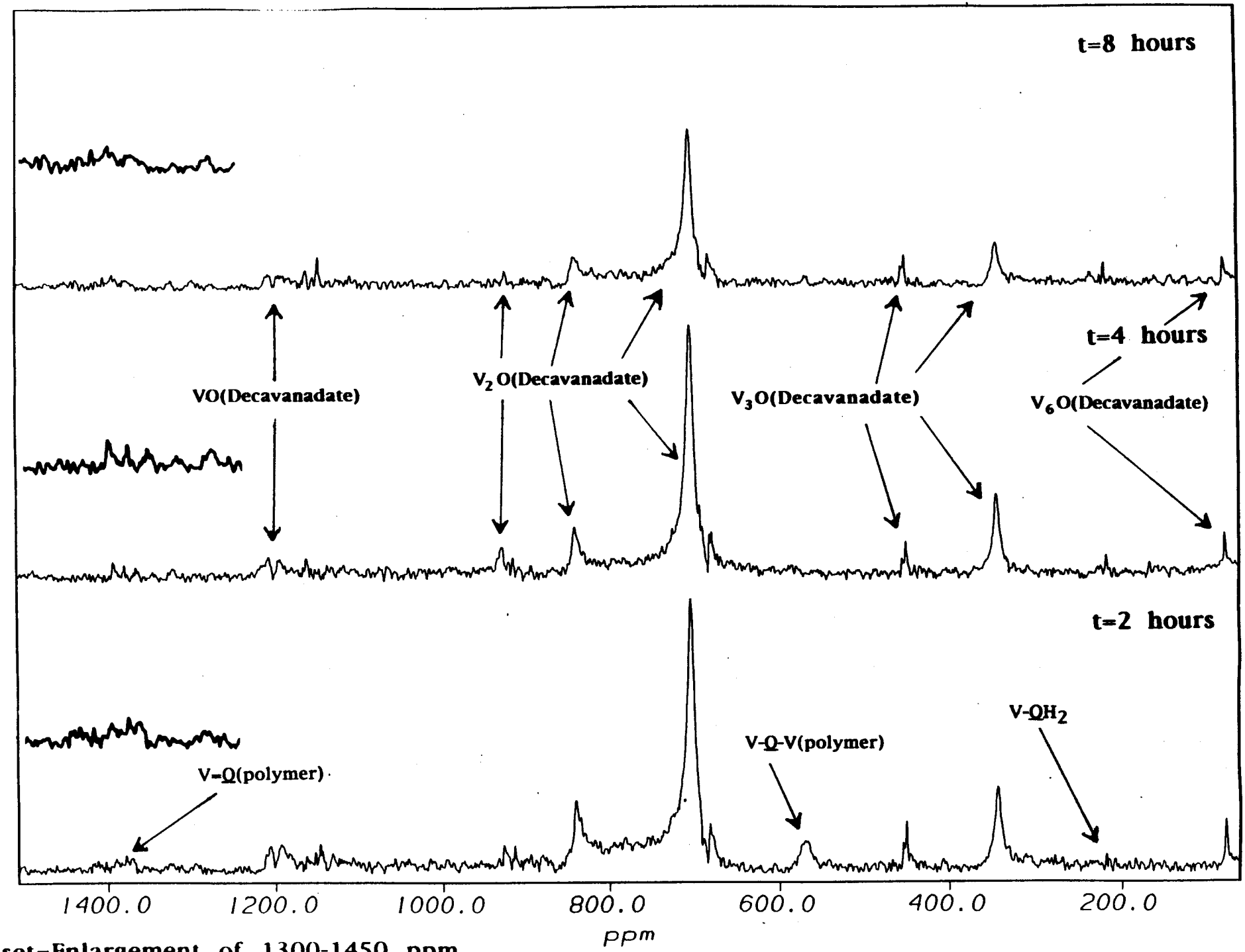


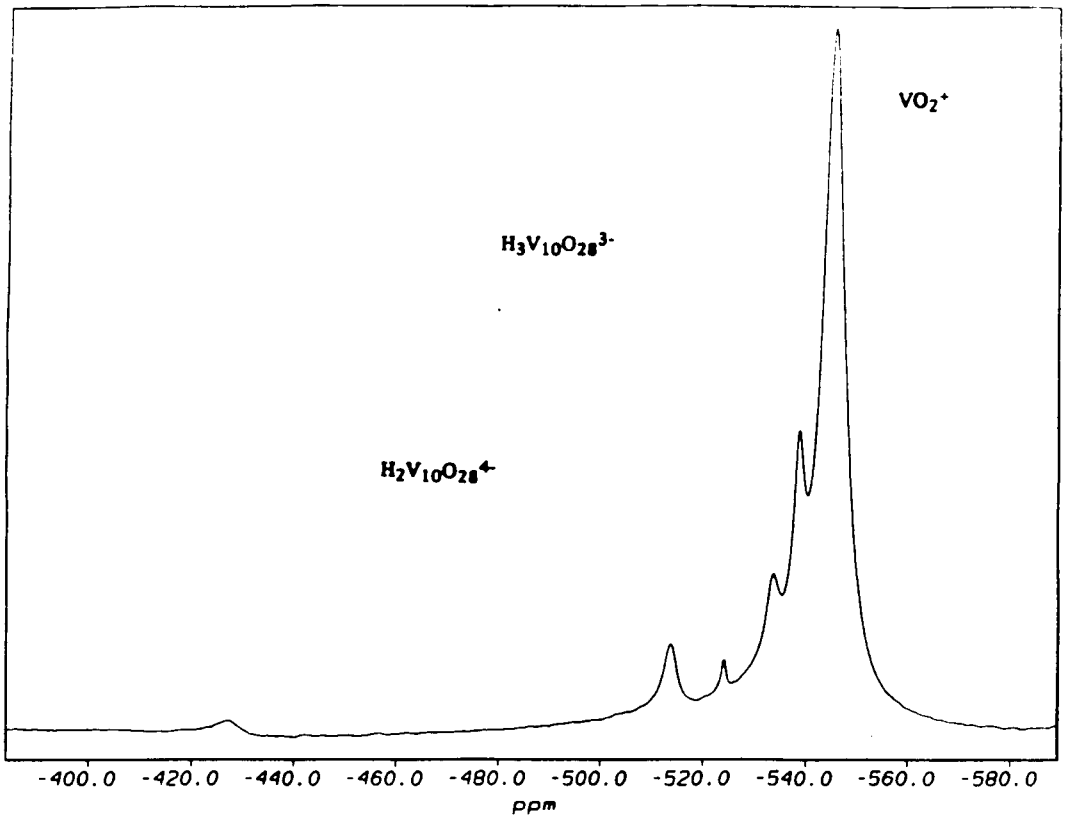
Figure 3. ^{17}O NMR of Reacting Solution



*Inset=Enlargement of 1300-1450 ppm

Figure 4.

^{51}V NMR of Solution Containing $VO_2(H_2O)_4^+$



^{17}O NMR of Solution Containing $VO_2(H_2O)_4^+$

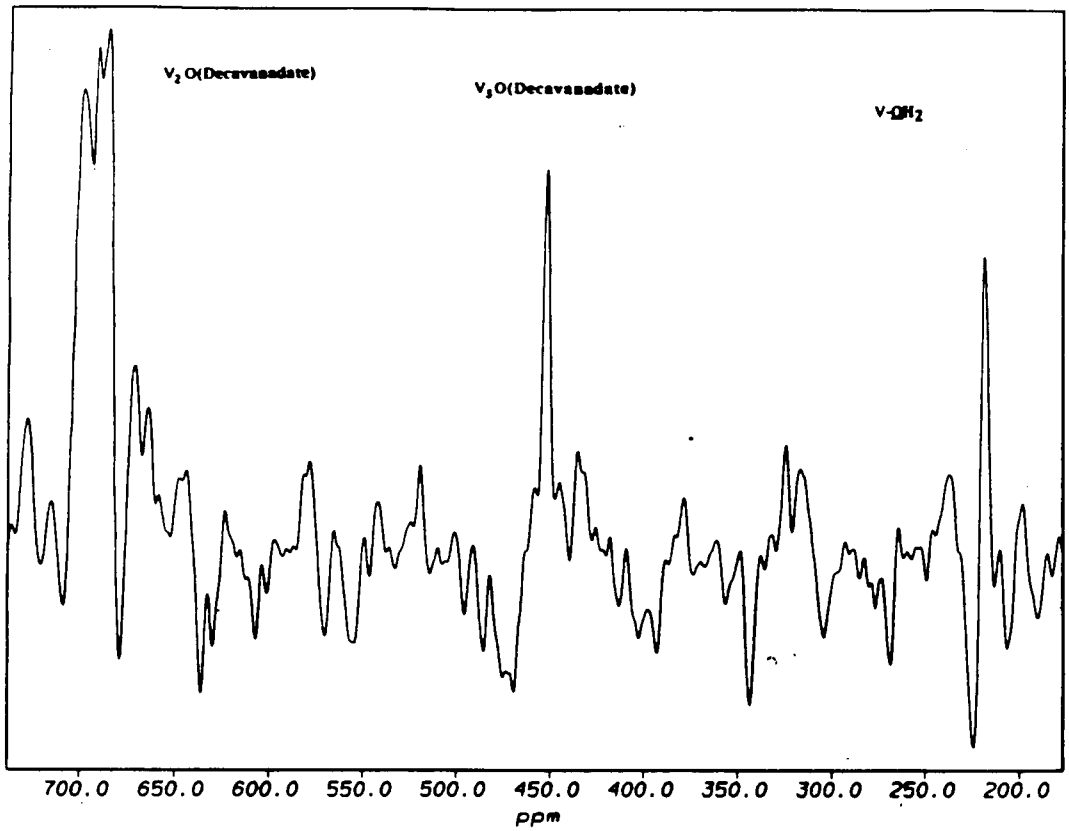


Figure 5. ^{51}V MAS NMR Spectrum of V_2O_5 Gel

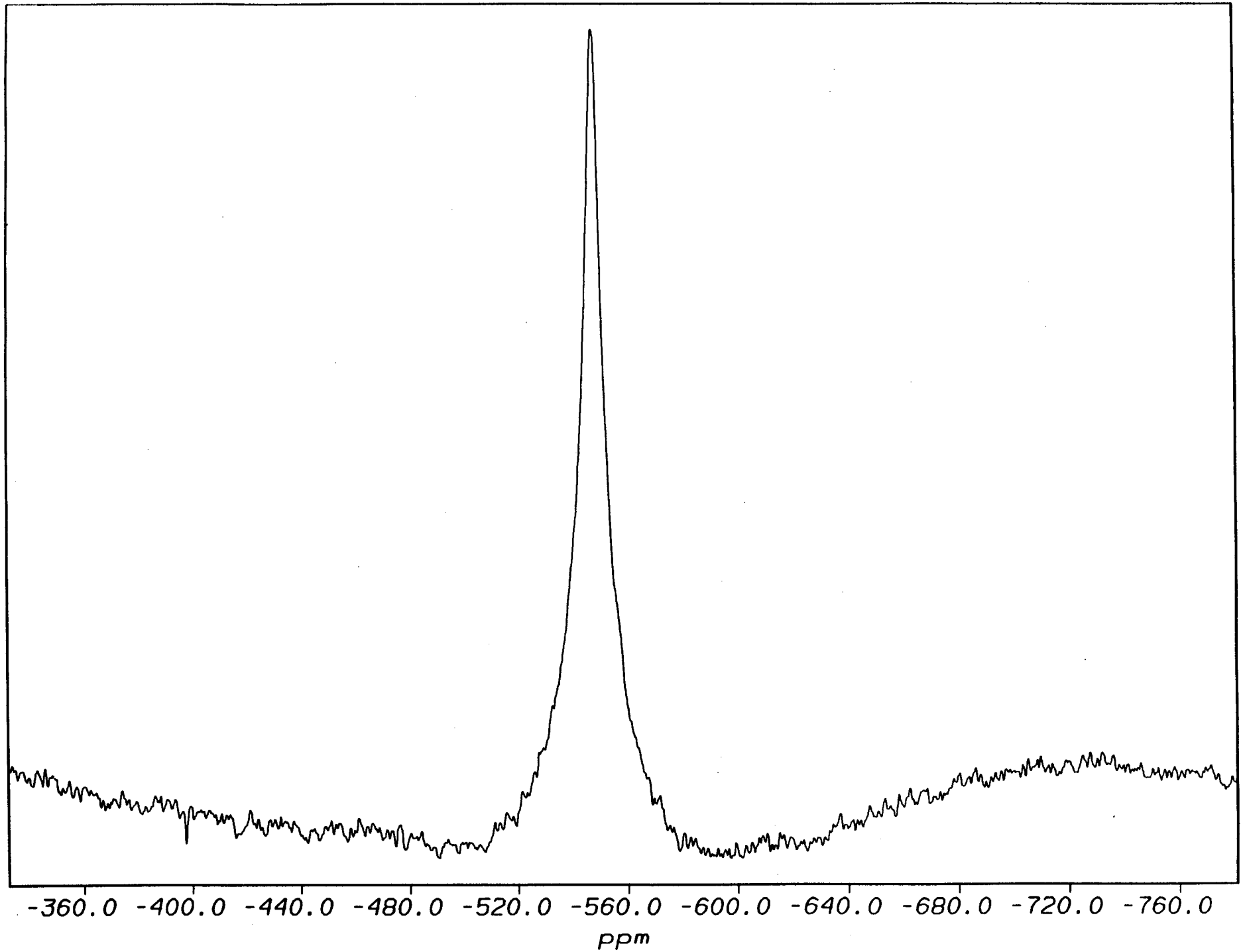


Figure 6. ^{17}O MAS NMR Spectrum of V_2O_5 Gel

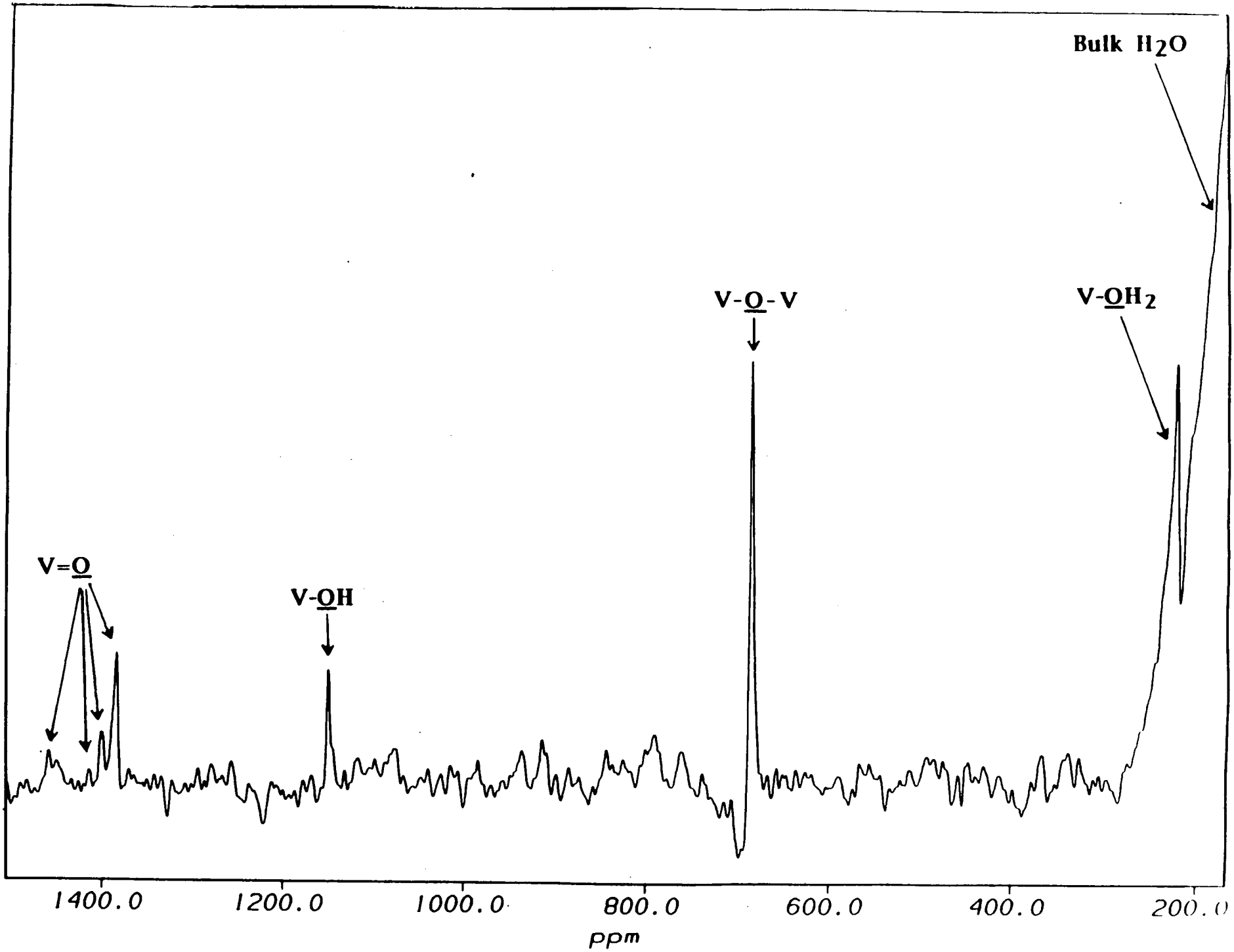


Figure 7. Repeat Unit in Vanadia Polymer

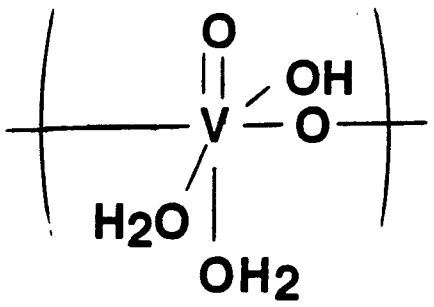
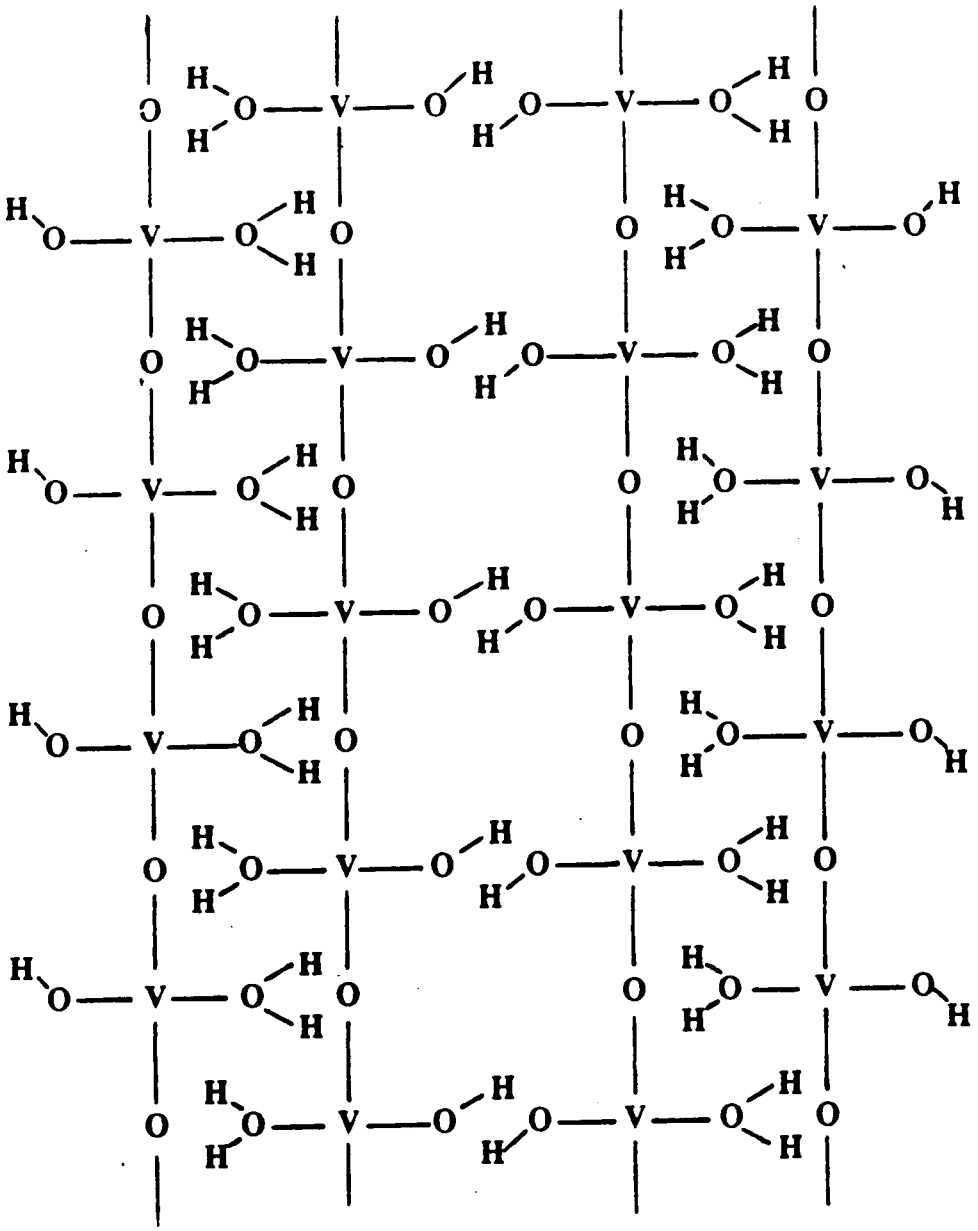
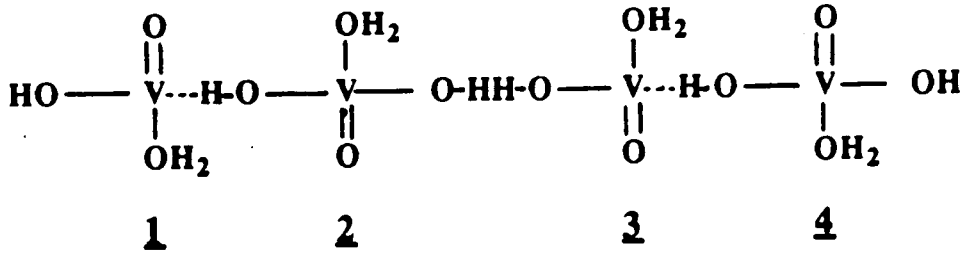


Figure 8. "Wet" Ribbon Structure

Top View of Ribbon



Planar View of Ribbon



Proposed Assembly of Hydrolyzed Linear Polymers into Ribbon Structure. Individual Chains are numbered for identification.

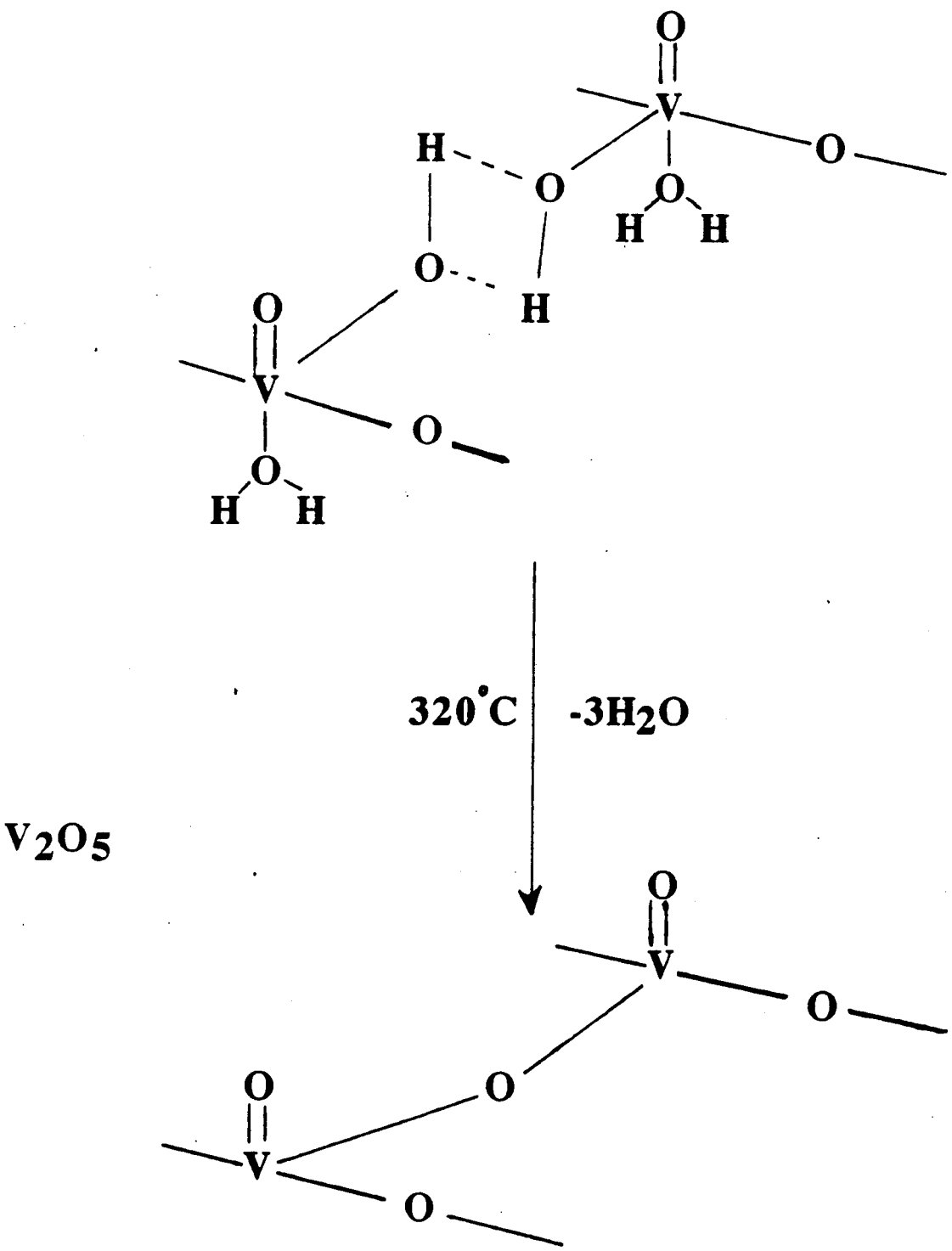


Figure 9. V_2O_5 Unit in Dried Gel