Evolution of V(V) Species and the Formation of V−O−Si Bonds during the Synthesis of Vanadia−Silica Sol−Gel Materials

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The solution chemistry of vanadium(V) species in an aqueous alcoholic silicate solution was studied by ^{51}V NMR spectroscopy. It was found that under conditions of low water, vanadium silicate species, containing V−O−Si linkages, formed immediately and remained at approximately steady-state concentrations during most of the reaction. At high concentrations of water, the oxovanadium triisopropoxide reacts quickly through hydrolysis and self-condensation to form vanadate species. The observation of these different species in solution provides a detailed, molecular-level interpretation of the factors that influence the formation of homogeneous, multicomponent vanadia−silica glasses made through the sol−gel process.

Introduction

Complexes of vanadium(V) in solution have been investigated rather extensively in recent years, both for their intrinsic chemical interest and for their relationship to specific biological systems.[1] In that respect, a number of excellent studies have been carried out, using ^{51}V NMR spectroscopy, to understand the reactions of vanadium complexes in solution and to elucidate their interactions with biologically relevant molecules.[2] A parallel interest in vanadium also exists in materials chemistry where, for example, vanadium(V) oxides in various forms comprise an important class of heterogeneous catalysts.[3] In recent years, the production of vanadium containing inorganic oxides through solution chemical techniques, such as the sol−gel process, has been of increasing interest due to the synthetic flexibility afforded by such approaches. Pure vanadia gels, useful for their semiconducting and antistatic properties, have been fabricated by the hydrolysis of vanadium(V) alkoxides.[4] Similarly, multicomponent systems consisting of vanadia dispersed in an oxide matrix such as silica or titania have been fabricated for their catalytic, semiconducting, and chemical sensing properties.[5]

Many of the useful properties of dispersed vanadia−silica xerogels arise from the nature of the vanadium sites distributed in the silica matrix. From studies of supported vanadia heterogeneous catalysts, these sites are known to be discrete pseudotetrahedral oxovanadium centers that have a short terminal vanadium oxygen bond and three basal-plane vanadium−oxygen−silicon linkages.[6,7] For optical applications, such as chemical sensing, the distribution of vanadium in the silica must be uniform so as to yield homogeneous, optically transparent bulk materials. In this regard, our own particular research into these materials has focused, in large part, on the specific chemical factors that effect the production of homogeneous xerogels. For example, it was determined that high initial water content resulted in the formation of heterogeneous opaque xerogels, in which the vanadia had self-condensed into a distinct, separate phase. Xerogels made with a low initial water content, however, remained homogeneous throughout the process. Even with low initial water concentrations, however, there was a limit on the amount of vanadium that could be incorporated while

maintaining homogeneity.[8] Although these observations are useful in suggesting synthetic protocols for the fabrication of homogeneous vanadia−silica materials, they provide little understanding, on a molecular level, of the chemical processes that give rise to these properties. This is significant because the nature of the vanadium species present in the sol−gel solution and the specific interactions of these species with solution phase silica should dictate the ultimate distribution of the metal in the matrix and the homogeneity of the final xerogel. To attain a more fundamental understanding of the underlying chemistry, we undertook an investigation of the primary sol−gel reactions in the presence of vanadium ions using ^{51}V NMR techniques. The results of that investigation are reported herein.

Experimental Section

Tetramethyl orthosilicate (TMOS; 99+%), oxovanadium triisopropoxide, and triethylsilanol were purchased from Gelest, whereas vanadium oxytrichloride (VOCl$_3$) was obtained from Aldrich. Methanol and 2-propanol were purchased from Fisher. Tetramethyl orthosilicate was refluxed over sodium methoxide and distilled under nitrogen. Oxovanadium triisopropoxide was fractionally vacuum distilled immediately prior to use. Methanol and 2-propanol were all refluxed over calcium hydride for 24 h under a nitrogen atmosphere and distilled immediately prior to use. In all distillations, a forerun comprising ∼10% of the total volume was collected and discarded, while a similar volume was left in the distillations flask at the end of the distillation. Only the intermediate fraction, collected at a constant temperature, was used in the experiments. Anhydrous methylcyclohexane was purchased from Aldrich and used as received. Oxovanadium tristriethylsiloxide and oxovanadium trimethoxide were synthesized following a literature procedure.[9] Samples for NMR spectroscopy were prepared under anhydrous conditions utilizing Schlenck techniques. The solutions were transferred to dried, septa-capped 10 mm NMR tubes under a constant flow of dry nitrogen using a gastight syringe.

Nuclear magnetic resonance experiments were performed on a Varian Unity Plus console operating at 720 MHz (for ^{1}H) NMR Spectrometer. The broadband probe was tuned to 139.9 MHz for the ^{51}V nucleus, and all of the spectra were collected

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at ambient temperature. Data were collected over 100 000 Hz sweep width using 32 704 points (with an acquisition time of 0.164 s), recycle delay 0.5 s using an ∼30° excitation pulse. The raw data were apodized by 50 Hz exponential line broadening prior to Fourier transformation. All of the [51]V NMR peaks were externally referenced to vanadium(V) oxytrichloride (VOCl₃).

UV−Vis spectra were collected on an On-Line Instruments Carey 14 conversion spectrometer. The spectra were collected as solution spectra in a 1 cm quartz cuvette. The solutions were prepared under scrupulously anhydrous conditions in an inert atmosphere environment using anhydrous methylcyclohexane as the solvent. The spectra were run against a pure solvent reference.

Results and Discussion

Control Experiments and Analysis of Chemical Shifts. The production of vanadia−silica xerogels can be accomplished by reacting a silicon tetraalkoxide and oxovanadium triisopropoxide with water, usually in an alcohol solvent.[5d]

$$mSi(OR)_4 + nOV(OR)_3 \rightarrow$$
$$[Si_mV_nO_{(2m+2.5n)}] + (4m + 3n)ROH \quad (1)$$
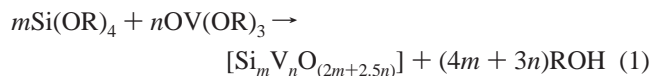
Under these conditions, the vanadium alkoxide would be expected to undergo a variety of reactions. For example, the transesterification of alkoxy groups, either from alcohols in solution or directly from the silicon alkoxide is known to be facile.[10] The addition of water results in hydrolysis of both the vanadium and the silicon alkoxides. Upon hydrolysis, vanadium alkoxides can self-condense to form V−O−V bonds. This can lead to the well-studied red polymeric vanadia gels or to discrete vanadates and isopolyvanadates, depending on the conditions.[4,11] Alternatively, the hydrolyzed vanadium and silicon can co-condense to form V−O−Si linkages. The occurrence of this last process is, of course, of primary concern in understanding the formation of dispersed vanadia−silica gels. Clearly, the variety of possible reactions that can occur in concert suggests that there could be considerable complexity to the vanadium species present in the sol−gel solution. As a consequence of this, we present first a brief discussion of the expected chemical shifts of oxovanadium−siloxide species. To the best of our knowledge, such an analysis has not been previously presented and an understanding of the expected shifts is important in assigning vanadium siloxide complexes in solution. This will be followed by control studies of alkoxide (methoxy/isopropoxy) and alkylsiloxide (triethylsiloxy/isopropoxy) metathesis in oxovanadium triisopropoxide. These controls will help in assigning such species as they form in the multicomponent sol−gel solution. These studies will be followed by investigations of the vanadia−silica sol−gel reaction itself.

Chemical Shifts of Oxovanadium Siloxide Complexes. Both solid-state and solution [51]V NMR spectra have been reported for vanadium species containing V−O−Si linkages.[7,12] The tris-(trialkyl)siloxy complexes of oxovanadium, OV(OSi(R)₃)₃, generally have [51]V NMR resonances significantly upfield from their trialkoxy analogues. For example, oxovanadium tris-(triethyl)siloxide has a resonance at −715 ppm compared to −673 ppm for the tri-*t*-butoxide. Factors affecting the [51]V chemical shift have been explained in some detail by Rehder using the Ramsey shielding equation.[13] For the case of pseudotetrahedral (C_{3v}) oxovanadium(V) complexes, it was found that, as the electronegativity of the pendant (X) group increased, the [51]V chemical shift moved progressively upfield. This was

demonstrated for the series of halides wherein OVBr₃, OVCl₃, and OVF₃ have chemical shifts of +432, 0, −700 ppm, respectively, relative to OVCl₃ itself.[13]
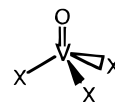
A similar pattern might be anticipated for the case of groups connected by bridging oxygens [X = LO−], where increases in the electronegativity of "L" should result in a upfield chemical shift. On the basis of these arguments, the upfield shift observed in going from carbon to less electronegative silicon appears to be somewhat anomalous.

The chemical shift, δ, is given by the expression $\delta = \sigma_o - \sigma$ where σ_o is the shielding constant of the reference (VOCl₃), and σ is the shielding constant of the compound. The major contribution to differences in shielding for these compounds is found to come from the local paramagnetic term.[14] This contribution to the shielding can be calculated from ligand field theory and is given in an approximate form by the expression below, where ΔE is the average excitation energy between the ground and the excited states, $\langle r^{-3} \rangle$ is the average orbital volume for the 3d orbitals, and k' is the orbital reduction factor, which, for the first transition series, is close to 1.[15,16,13]

For a homologous series of pseudotetrahedral vanadium complexes, the

$$\sigma_{para} \propto -\overline{(\Delta E)^{-1}} \langle r^{-3} \rangle_{3d} k'^2 \quad (2)$$

dominant factor in this expression is usually $(\Delta E)^{-1}$, the reciprocal of the average ground-to-excited-state energy gap. The correlation of the chemical shift to the average electronic transition energy or quantities related to it, such as the calculated one-electron HOMO−LUMO gap, are often very good.[13,17] For pseudotetrahedral oxovanadium complexes, the highest occupied molecular orbitals are nonbonding 2p orbitals localized on the pendant ligands, and the lowest unoccupied molecular orbitals are antibonding "d" orbitals localized on the metal. Because electronic transitions between these orbitals are charge-transfer in nature, the energy will increase as the pendant atoms become more electronegative, thereby making the 2p electrons more difficult to ionize. This explains the observed upfield [51]V NMR shift with increasing electronegativity.[13,17] For the case of bridging oxygens, X = RO−, R₃SiO−, (RO)₃SiO−, (≡SiO)₃SiO−; (R = alkyl), an analogous situation will exist with lone-pair electrons on the oxygen constituting the HOMO. This is confirmed for the case of pseudotetrahedral oxovanadium bonded into silica xerogels, where spectroscopic studies have shown that the lowest energy excited state is a ³E state arising from the promotion of an electron from an a₂ nonbonding orbital on the oxygen to an e symmetry antibonding orbital on the metal.[18] The energy of the oxygen 2p orbitals would, in turn, be modulated by the electronegativity of the group bonded to it. On the basis of these arguments, the replacement of carbon with less electronegative silicon would be expected to decrease the energy gap and shift the [51]V NMR resonance downfield and not upfield as is, in fact, observed.

Notwithstanding the lower electronegativity, the average electronic energies of siloxy bound vanadium lies to higher energy than the alkoxy analogue. This can be seen in the electronic spectra of oxovanadium triisopropoxide and tris-(triethyl)siloxide (Figure 1), which clearly shows a blue shift
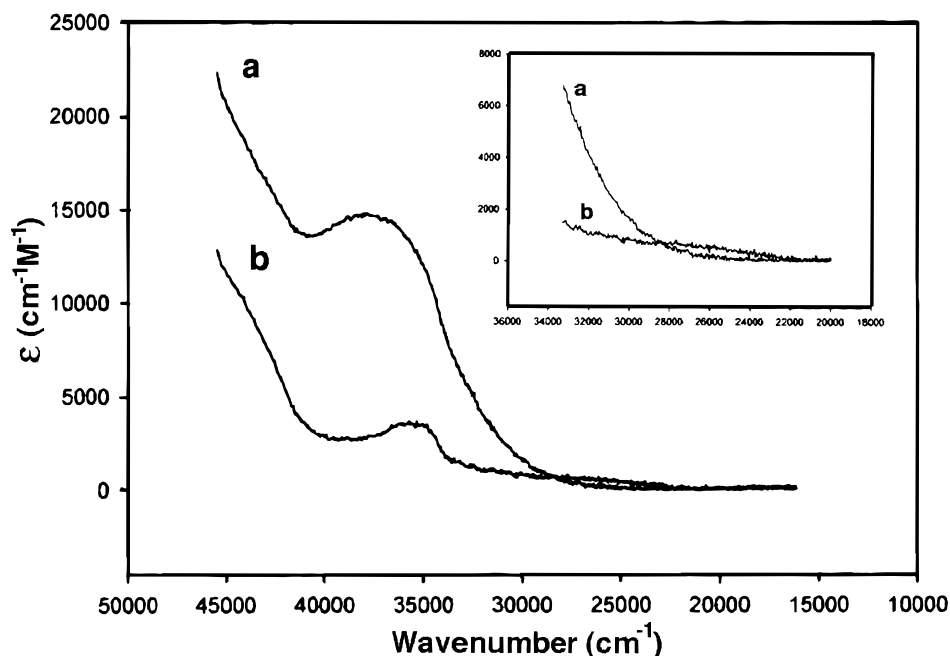
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Figure 1. UV-Vis spectra of (a) oxovanadium tris(triethyl)siloxide and (b) oxovanadium triisopropoxide in methylcyclohexane.

in the primary spectral features in going from silicon to carbon. These spectra show intense bands at 37 879 and 35 714 cm^{-1} for the triethylsiloxy and isopropoxy complexes, respectively. By the analogy to silica bound pseudotetrahedral oxovanadium, these intense bands can be assigned to $^1A_1 \rightarrow {}^1A_1$ charge transfer transitions localized primarily on the terminal V=O bond.[18] Transitions from the bridging oxygen ligands, which constitute the HOMO, to the metal localized LUMO ($^1A_1 \rightarrow {}^{1,3}E$) are much weaker and to lower energy. These transitions are observed in the electronic spectrum of the triisopropoxide complex (Figure 1, inset) which shows a broad weak band centered around 26 316 cm^{-1} and extending down to around 22 727 cm^{-1}. No evidence of transitions in this region is observed in the tris(triethyl)siloxy complex, even at elevated concentrations. This suggests that the analogous transitions for this complex are contained under the low-energy edge of the strongly allowed 37 879 cm^{-1} transition, which starts to gain intensity at $\lambda \sim 26\,667$ cm^{-1}. Regardless of the exact nature of the electronic transitions, it is clear that the average energy is distinctly blue shifted in going from the alkoxy to the siloxy complex. This blue shift is not entirely unexpected and results from the ability of silicon and other second row elements to increase the energy of the 2p electrons on the oxygen. This has traditionally been assigned as a pπ−dπ interaction between empty 3d orbitals on the silicon and 2p electrons on the oxygen however recent studies have indicated that such interactions are unlikely.[19,20]

Alkoxide Metathesis of Oxovanadium Trialkoxides. The ^{51}V NMR resonances for oxovanadium trialkoxides occur over a relatively large chemical shift range and have been discussed in some detail by Rehder.[21] Oxovanadium trialkoxides with large, sterically demanding alkoxy groups such as *iso*-propoxy and *tert*-butoxy have sharp resonances with chemical shifts well upfield from the reference, VOCl$_3$, (−631 and −673 ppm respectively).[21,22] Conversely, smaller, less sterically demanding alkoxy groups, such as ethoxy and methoxy, have broad resonances that occur further downfield. This broadening and concomitant downfield shift is attributed to rapid ligand exchange at the metal center and to the tendency of these complexes to increase their coordination number through dimerization or oligomerization.[23]

For the sol−gel process, the concentration of vanadium will be relatively high and the sterically bulky isopropoxy groups can exchange with the less sterically demanding methoxy group from TMOS, either directly or from the alcohols liberated by their hydrolysis.[10] This suggests that, at least initially, mixed alkoxy vanadium species are likely to be present in the spectra. To understand where the ^{51}V NMR resonances of mixed alkoxide is likely to occur under typical sol−gel conditions, solutions of oxovanadium triisopropoxide (20 mM) were made with methanol-to-2-propanol ratios that mimic the early stages of the process. In particular, addition of methanol (0.6 M) to 2-propanol (13 M) produces a relatively sharp resonance downfield from the triisopropoxy complex at −612 ppm (Figure 2b). As the amount of methanol increases (12 M) relative to 2-propanol (6 M), a second peak appears even further downfield at −592 ppm. It appears reasonable to assign these peak to methoxy substitution products with the band at −612 ppm being the monosubstituted species, OV(OPr^i)$_2$(OMe), whereas the band further downfield at −592 ppm is the disubstituted species OV(OPr^i)(OMe)$_2$. These assignments must be taken with considerable caution. The bands are broad indicating chemical exchange processes and the possibility that the resonaces represent a coalescence of resonances of several different species. The spectra collected at 273 K show a sharpening of the bands and a change in the chemical shift of the two downfield resonances to −609 and −582 ppm, respectively, but no resolution of the spectrum into more bands is observed. Irrespective of specific band assignments, these spectra indicate the position at which simple alkoxide metathesis products are likely to be observed during the multicomponent sol−gel process.

Model Systems of Silanol Substitution of Vanadium Alkoxides. The ^{51}V NMR spectra of 2-propanol solutions of oxovanadium triisopropoxide in the presence of triethylsilanol in mole ratios of 0.5:1, 1:1, and 2:1 are shown in Figure 3. At a 0.5:1 mole ratio, the spectrum shows the appearance of three new peaks upfield from the −631 ppm resonance of the oxovanadium triisopropoxide at −654 and −681 and −714 ppm. As the silanol:vanadium ratio increases, no new resonances appear, but the intensities of the −681 and −714 ppm bands become
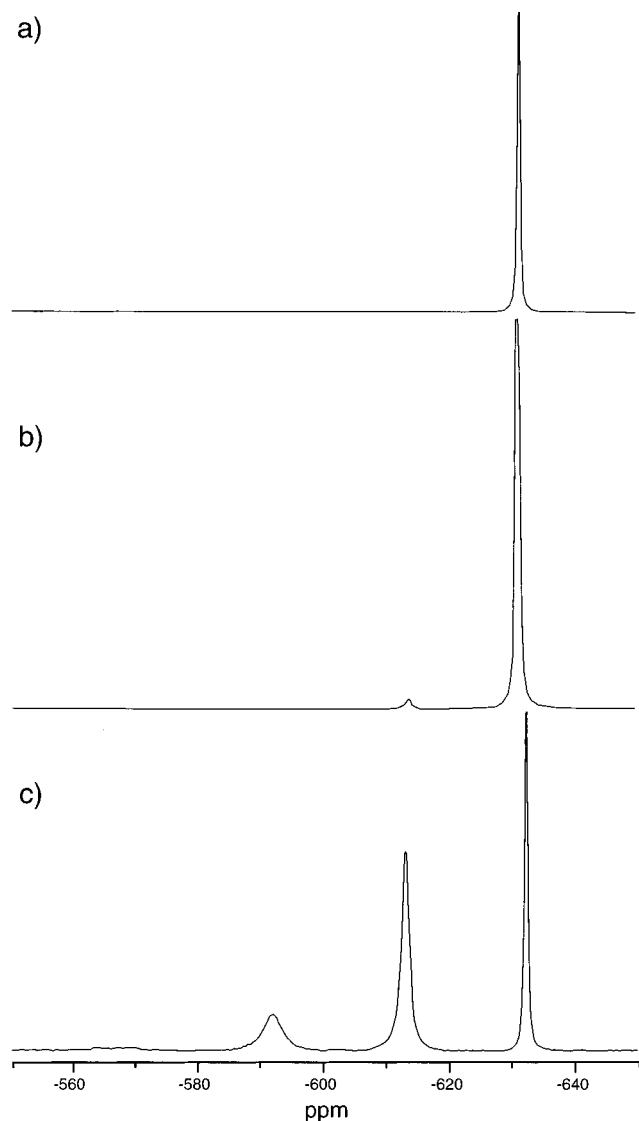
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a)

b)

c)

a)

b)

c)

d)

Figure 2. ^{51}V NMR spectra of a (a) 0:1, (b) 0.025:1, and (c) 1:1 methanol/2-propanol (v/v) solution of oxovanadium triisopropoxide (20 mM).
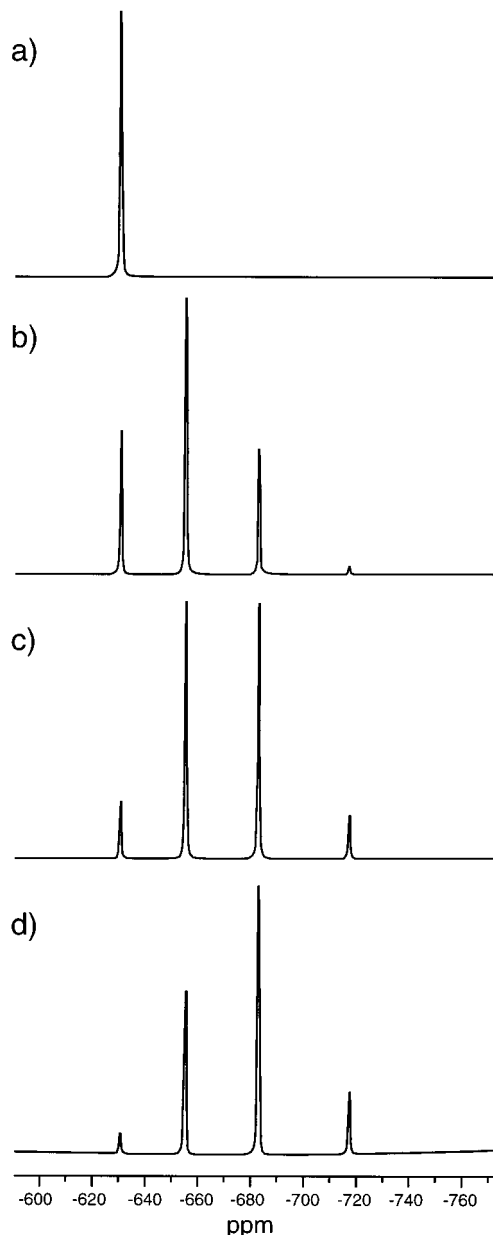
Figure 3. ^{51}V NMR spectra of a 2-propanol solution of oxovanadium triisopropoxide (20 mM) with triethylsilanol in mole ratios of (a) 0:1, (b) 0.5:1, (c) 1:1, and (d) 2:1 Si:V.

larger relative to the −631 and −654 peaks. The peak at −714 ppm corresponds to oxovanadium tris(triethyl)siloxide, (Et$_3$SiO)$_3$VO, as determined from an authentic sample. We therefore assign the intermediate peaks at −681 ppm and −654 ppm to the mixed alkoxy/siloxy species, OV(OPr^i)(OSi(Et)$_2$) and OV-(OPr^i)$_2$(OSi(Et)), respectively. To simulate the complex substitutional process that is likely to go on in the early stages of the sol−gel process, small amounts of methanol were added to a 2-propanol solution containing 1:1 molar solution of oxovanadium triisopropoxide and triethylsilanol (Figure 4). The spectra show a peak at −612 ppm corresponding to methoxy exchange with the triisopropoxy parent complex and two peaks approximately 20 ppm downfield from each of the siloxy substituted complexes at −636, and −661 ppm. We assign these resonances to methoxide substitution of the mono and disiloxy complexes to form OV(OMe)(OSi(Et)$_3$)$_2$ and OV(OPr^i)(OMe)-(OSi(Et)$_3$). At the low concentrations of methanol used, we do not observe a resonance assignable to the dimethoxy species OV(OMe)$_2$(OSi(Et)$_3$), which would be expected to occur around −618 ppm.

Studies of The Vanadia−Silica Sol−Gel System. The ^{51}V NMR of a 10.3 mM solution of oxovanadium triisopropoxide and tetramethyl orthosilicate (0.5 mol % V; (V/V+Si)) in

2-propanol is shown in Figure 5. Along with the the peak of the parent triisopropoxy complex at −631 ppm, a very weak structured resonance is observed upfield at −662 ppm, whereas a single, weak feature is observed downfield at −612 ppm, which corresponds to methoxide metathesis of the oxovanadium triisopropoxide, as was discussed previously (Figure 2). The addition of water in quantities used in the sol−gel process (3:1 H$_2$O:Si) results in the a decrease in the parent peak at −631 ppm and a dramatic increase in the band centered around −662 ppm, which is now well resolved into a number of narrowly spaced resonances. In addition, another cluster of intense sharp peaks emerge further upfield around −700 ppm. Approximately 20 ppm downfield from each of these groups of strong peaks are weaker resonances at −642 and −680 ppm, respectively, which also show fine structure (see expansion, Figure 5d). As the spectrum evolves over a 30 min time interval (Figure 5), the intensities of all the downfield peaks increase, whereas the parent triisopropoxide band decreases. At the end of this period,
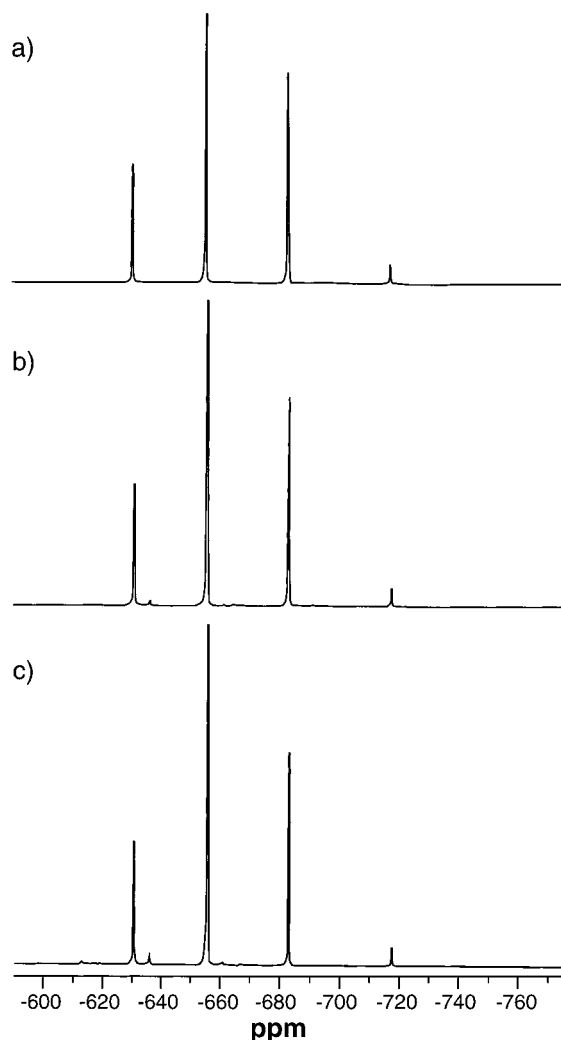
Figure 4. ^{51}V NMR spectra of a 2-propanol solution of oxovanadium triisopropoxide (20 mM) with triethylsilanol in a 1:1 Si/V mole ratio of with (a) 0:1, (b) 6:1, and (c) 10:1 mol of methanol/moles of V.

Figure 5. ^{51}V NMR spectra of oxovanadium triisopropoxide (20 mM) and tetramethyl orthosilicate (2.05M) in 2-propanol (a) initially, (b) 2 min, (c) 15 min, and (d) 30 min after addition of three equiv of water (3:1 H$_2$O/Si).

a weak resonance emerges well upfield from all the other resonances at −758 ppm.

By analogy to the triethylsilanol system, and considering the time evolution of the spectra, we assign the resonances in the region of −662 and −700 ppm to the mono- and disiloxide metathesis products of oxovanadium triisopropoxide, OV(OPr^i)$_2$-(OSi≡) and OV(OPr^i)(OSi≡)$_2$, respectively. The direction of the chemical shift, which is upfield from the triethylsilanol analogue, is expected because the (MeO)$_3$Si— group should be more electronegative than the (Et)$_3$Si— group. As with triethylsilanol substitution, the upfield chemical shift between successive substitutions is not constant, but increases with increasing degrees of substitution. It is possible that the weak resonance at −758 ppm is the trisubstituted product, OV(OSi-(OSi≡)$_3$)$_3$, which, due to large steric congestion, does not form in appreciable concentrations. However, its upfield shift is significantly larger than would be anticipated from the silanol model study. Finally, we attribute the small amounts of methoxide (−612 ppm) ion prior to the addition of water to the presence of trace amounts of hydrolysis of the TMOS. Solutions made directly after distillation of the starting materials showed minimal amounts of these reaction products, but they were never entirely removed. This control sample then, in effect, provides information about the products formed under a very limited extent of reaction.
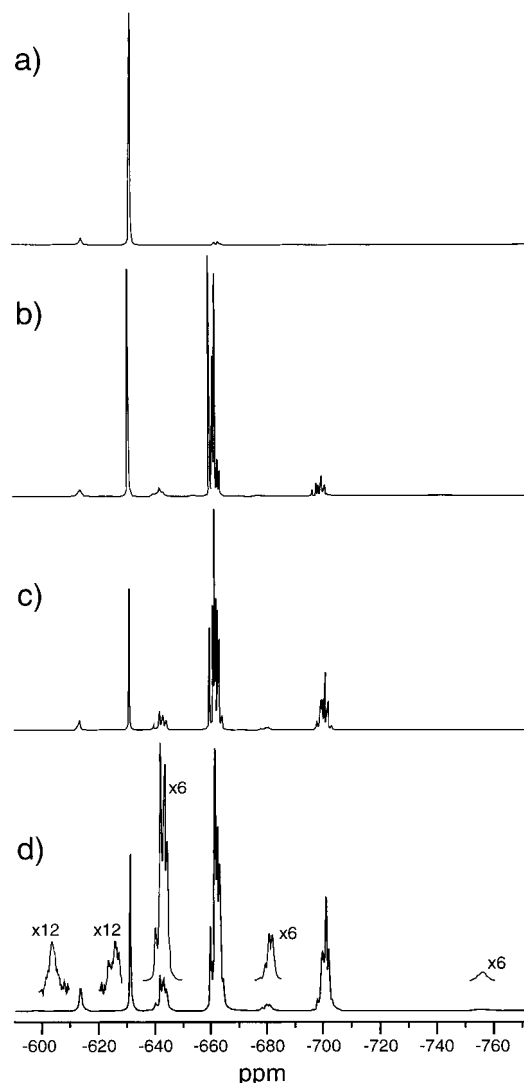
Each of the two primary resonances (−662 and −700 ppm) is accompanied by a weaker resonance appearing at ∼20 ppm downfield. We assign these to alkoxide exchange in the mono- and disubstituted oxovanadium siloxides. Specifically, OV(OPr^i(OMe)(OSi(OSi≡)$_3$) and OV(OMe)$_2$(OSi(OSi≡)$_3$) for the mono- and OV(OMe)(OSi(OSi≡)$_3$)$_2$ for the disiloxide. Several things are consistent with such an assignment. The peaks increase over time as more methanol is produced, and, as can be seen from the expansion (Figure 5d), the fine structure closely mirrors that of the primary resonance. In addition, the downfield shift is approximately the same as that which is observed for methoxide substitution in oxovanadium trisopropoxide. For the oxovanadium monosiloxide complex, there are two possible substitution products, OV(OPr^i)(OMe)(OSi(OSi≡)$_3$) and OV-(OMe)$_2$(OSi(OSi≡)$_3$). On the basis of substitution studies in mixed alcohol solutions, it would be anticipated that the higher substituted species would yield a resonance even further downfield. In fact, further expansion of the spectra (Figure 5d) reveals a very weak but structured resonance at −626 ppm that we attributed to these species. For OV(OMe)(OSi(OSi≡)$_3$)$_2$, only one species would be expected and only one is observed.

Figure 6 shows the expansion of the spectral region around −662 ppm for the temporal evolution of the reaction at 3:1
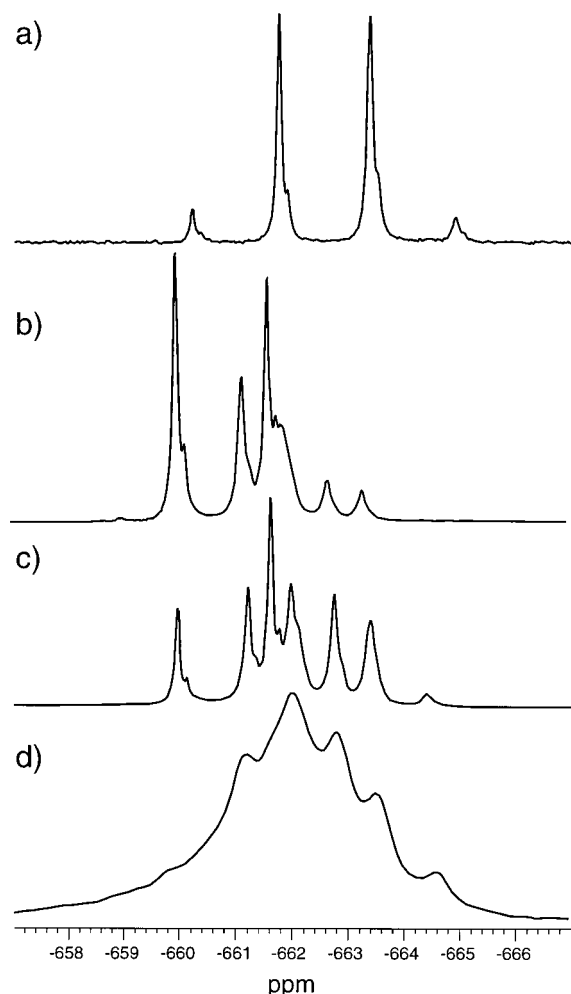
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Figure 6. Expansion of the[51]V NMR spectrum over a spectral region from −657 to −667 ppm of oxovanadium triisopropoxide (20 mM) and tetramethyl orthosilicate (2.05M) in 2-propanol (a) initially, (b) 2 min, (c) 10 min, and (d) 3 h after addition of three equiv of water (3:1 H_2O/Si).

Figure 7. [51]V NMR spectra of oxovanadium triisopropoxide (20 mM) and tetramethyl orthosilicate in 2-propanol (a) initially, (b) 10 min, (c) 90 min, (d) 5 h, and (c) 10 h after addition of water at 8:1 H_2O/Si.

H_2O:silicon. As can be seen from the spectra, this resonance consists of a number of sharp, closely spaced lines separated by ∼0.5−1.6 ppm. These splittings are field dependent and their number and intensity changes significantly over time. In the initial spectrum (Figure 6a), where a very limited amount of reaction has occurred due to trace water in the solution, four equally spaced peaks are observed 1.6 ppm apart. Immediately after the addition of water, several of these peaks go away (particularly those upfield), and a number of new bands grow in. After addition of water, a broad distribution of peaks between −659 and −665 ppm emerges over time. A reasonable assignment for this fine structure is that it originates from hydrolysis and condensation products of the alkoxide groups on the vanadium bound siloxide: $OV(OPr^i)_2(OSi(OH)_x(OMe)_y(OSi$-$(O\equiv)_3)_z)$ $(x + y + z = 3)$. Certainly, the magnitude of the splitting is consistent with such a remote interaction. In addition, species resulting from the direct hydrolysis of the substituted vanadium may also be present. This would suggest that the evolution of the fine structure is indicative of the growth of the silica network pendant to the vanadium. As the silica system becomes more extensive and therefore more remote from the vanadium, we would expect the spectrum to converge to a single resonance. This is observed (Figure 6d) with spectra taken 3 h after the addition of water showing a general broadening and convergence to a single resonance centered around −662 ppm.
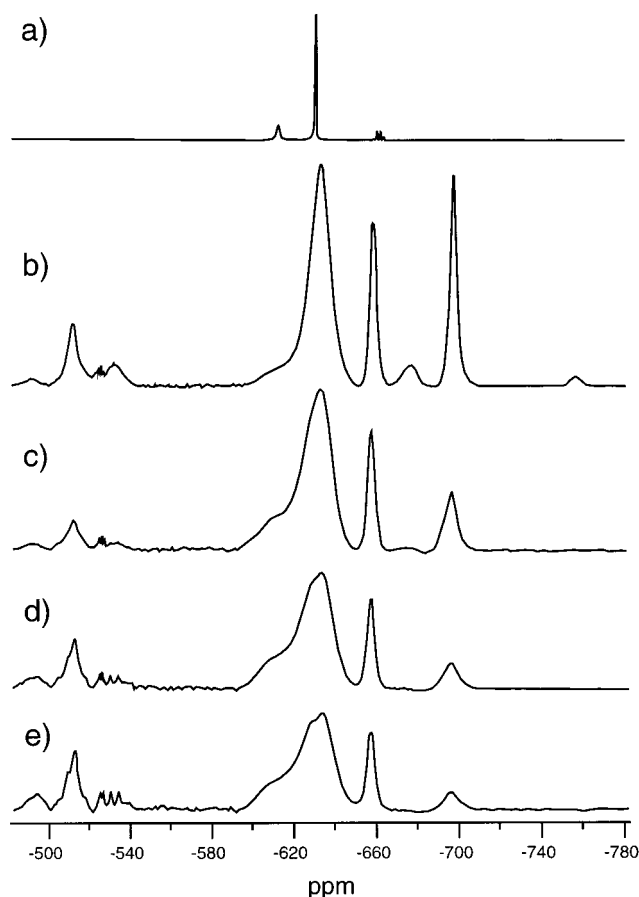
Increasing the water concentration for a fixed concentration of vanadium resulted in dramatically different temporal [51]V NMR spectra (Figure 7). Immediately after the addition of water at an 8:1 H_2O:silicon ratio, extensive reaction is observed. In comparison to the low water case, all of the observed resonances tend to be broad, indicative of rapid exchange processes. Peaks appear corresponding to mono- and disiloxide substitution (−659 and −698 ppm) and around the parent triisopropoxide complex at −634 ppm. They are, however, significantly broadened presumably due to exchange processes induced by the large amount of water. More interestingly, a complex group of resonances that are never observed at low water appear far downfield between −500 and −550 ppm. Over a relatively short period of time, the upfield bands associated with discrete V−O−Si species begin to disappear, whereas the resonances far downfield increase somewhat in intensity. Also emerging over time are several broad resonances between −590 and −640 ppm that appear initially as a shoulder on the −634 ppm peak.

The resonances at −628 and −634 ppm in the vicinity of the parent oxovanadium triisopropoxide (−631 ppm) appear to be exchange broadened, direct hydrolysis products of the parent complex. However, the addition of water to a solution of oxovanadium triisopropoxide in 2-propanol or mixed methanol/ 2-propanol solvents does not reproduce this resonance. This may suggest, but certainly does not prove, the involvement of silica species. The position and broadness of the bands between −500 and −550 ppm (Figure 8) suggests that these species are vanadates formed from complete hydrolysis and self-association at high water concentrations. Although a number of excellent studies have been carried out on aqueous vanadate solutions,
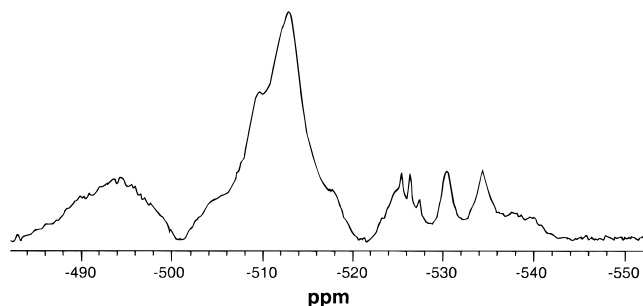
Figure 8. Expansion of the [51]V NMR spectrum of oxovanadium triisopropoxide (20 mM) and tetramethyl orthosilicate in 2-propanol 10 h after addition of water at 8:1 H_2O/Si in the region of −480 and −550 ppm.

there is no one-to-one correspondence between the chemical shifts of specific well-defined vanadates measured in those studies and the species we observe in the sol−gel solution. In general, most of the chemical shifts for aqueous vanadates have been reported for basic solutions. In the sol−gel solution, the pH is quite low (measured values of 1.5−2.0) and, more importantly, the solutions are highly nonaqueous and coordinating. As a result, the chemical shifts we observe are further downfield than those observed for simple vanadates in aqueous solution.[24] For example, the spectrum shows a series of three sharp lines at −525, −526, and −527 ppm and two broader resonances at −530 and −535 ppm that are well downfield from aqueous vanadate monomers, dimers, trimers, tetramers, and pentamers.[24] Notwithstanding this, the two peaks at −512 and −494 ppm are at the appropriate position and have the correct relative intensities to be assigned with some confidence to decavanadate, $V_{10}O_{18}^{6-}$. Though not explicitly shown in the scan window displayed in Figure 8, a weak resonance is observed at −420 ppm that is also consistent with this species. This may indicate that other isopolyvanadates or higher order oligomers may be present.[25] Finally, the [51]V NMR of several vanadosilicates (e.g., $O_3VOSiO(OH)_2^{3-}$) have been reported, also under basic conditions, and their resonances fall in the region from −564 to −603 ppm. As with the simple vanadates, this is somewhat upfield from the peaks we observed.[26]

As the sol−gel process proceeds and approaches the gelation point, the intensities of all the [51]V resonances continue to decrease. This is undoubtedly due to the incorporation of the vanadium into to the polysilica network. For the materials made at high water, the [51]V NMR resonances are almost gone by 4 days, well before gelation. In this case, reduction processes that accompany the formation of heterogeneous phases in the final gels may also be commencing. For the materials made with low water (Figure 9), the resonances assigned to the mono- and disiloxy oxovanadium species (−659 and −698 ppm respectively) slowly vanish as the process approaches gelation. As the gelation point is reached, all of the disiloxy complex is gone, whereas some of the monosiloxy complex remains. More interestingly, the sharp resonance for the parent triisopropoxy oxovanadium complex actually increases in intensity over time so that, at the gel point, some of the starting complex remains fluid in the pores.

An important point about these systems is that the vanadium is in dynamic equilibrium with the silica. The addition of excess water to solutions that were initially made at 3:1 water:silicon immediately generates the products observed at high water (Figure 8). This suggests that the V−O−Si bonds formed are hydrolytically labile and that the steady-state concentrations of mono- and di-trialkoxysiloxane oxovanadium complexes detected are favored because of the suppression of the hydrolytic
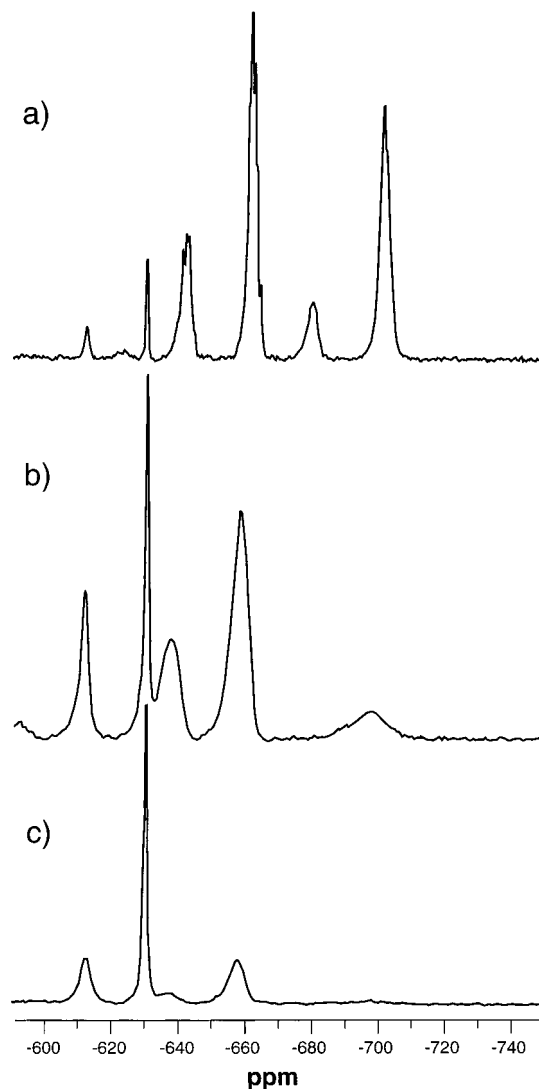

Figure 9. [51]V NMR spectra of oxovanadium triisopropoxide (20 mM) and tetramethyl orthosilicate (2.05M) in 2-propanol (a) 1, (b)5, and (c) 12 days after addition of three equiv of water (3:1 H_2O/Si).

back reaction at low water. Such behavior was also observed by Delattre and Babonneau for Ti(IV) and Zr(IV) interactions with silica.[27] This raises a significant question about the effectiveness of prehydrolysis of the silica in the production of homogeneous metal silica xerogels. Prehydrolysis is usually accomplished by first reacting the silica with a substoichiometric amount of water. The metal alkoxide is then added along with enough water to drive the reaction to completion. It is argued that this procedure overcomes the large kinetic mismatch between silicon and metal alkoxide hydrolysis rates thereby allowing the metal to react directly with partially reacted silica oligomers.[28] Detailed studies by McCormick of the alumina−silica system have shown that this is essentially valid for that system though the chemistry is more complex than most descriptions of prehydrolysis indicate.[29] In the case of early transition metals, the NMR experiments indicate that any Si−O−M bonds that form between metals and prehydrolyzed silica species will be readily reversed upon addition of water. This will place the metal ions back in solution, which would appear to overcome any kinetic advantage that this procedure might afford (though some advantage might be gained by the fact that some of the water is already consumed prior to the addition of the metal). In a previous study of the vanadia−silica system, Lee et.al. observed no formation of V−O−Si

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linkages between prehydrolyzed silica sols and vanadium isopropoxide, though appreciable alkoxide exchange took place.[30] These authors also observed that subsequent addition of excess water caused self-condensation of the vanadium and, under certain conditions, precipitation.

Conclusion

There are several significant observations that can be drawn from this previous work and our current study concerning the chemical factors that affect the production of multicomponent vanadia−silica glass. Running the sol−gel reaction under conditions of low water strongly shifts the system toward the formation of V−O−Si linkages. Although these species are hydrolytically labile, especially in the early stages of the reaction, the experiments suggest that, at low water, they remain in an essentially steady-state concentration until consumed into the silica polymer. It is for this reason that homogeneous materials with the vanadia discretely dispersed are produced under these conditions. Notably, however, oxovanadium tri-alkoxide complexes remain as discrete molecular species until after the gelation point, suggesting that some of the vanadium does not incorporate into the silica matrix until very late in the process. At high water content, the vanadia−silica interaction is diminished and oligomerization of the vanadia with itself dominates as suggested by the presence of vanadates. This is consistent with previous studies in which heterogeneity appears to arise through the partial reduction of vanadia gels formed in the process.[8] At high water concentrations, all solution phase vanadia species appear to be largely gone well before gelation. Clearly, these studies give a molecular interpretation to the origin of bulk properties found in vanadia−silica xerogels as a result of small changes in processing conditions. This suggests that understanding these processes at a molecular level can greatly increase our ability to dictate their final properties.

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