Synthetic Control over the Production of Multicomponent Sol−Gel Materials: Fabrication of Homogeneous Vanadia−Silica Xerogels with High Vanadium Content

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The effect of Brønsted acid catalysts on the gelation times and final homogeneity of vanadia−silica sol−gel derived glass is reported. It was found that the addition of hydrochloric acid reduced the gelation times, especially at high acid concentrations. This acid also caused slow reduction of the V(V) to V(IV) during the process. Drying of the V(IV)-containing xerogels at 500 °C resulted in their reoxidation to V(V). Characterization of the reoxidized gels by Raman and ^{51}V solid-state NMR spectroscopies verified that the structure of the vanadium(V) sites that were created from the reoxidation of the V(IV) sites were of pseudotetrahedral geometry with a short terminal oxo group and three Si−O−V linkages. This is the same site produced from direct incorporation of oxovanadium(V) into the gel without reduction occurring. A benefit is realized in this reduction−reoxidation process in that relatively high loadings (12.3 mol % or 17 wt % V_2O_5) of vanadium can be incorporated into the silica matrix while homogeneity is still maintained. Use of nonreducing acids such as HNO_3 resulted in no particular gains in vanadium loading, and in fact, materials produced with this acid were similar to those made with no added acid. The transition between homogeneous and heterogeneous materials is also discussed.

Introduction

The sol−gel preparation of multicomponent materials composed of transition metals dispersed in a silica matrix has been the subject of considerable recent attention.[1] This interest has been spurred by the broad potential uses for these materials in applications ranging from heterogeneous catalysis, optics, electronics, and chemical sensing.[2,3] For many applications, the useful properties of these materials arise from the uniform, homogeneous distribution of the metal through the silica gel matrix.[4] This homogeneity can be difficult to achieve with the sol−gel process, due to large differences in reaction rates between the metal alkoxides and the silicon alkoxides that form the matrix.[5] Notwithstanding this fact, careful control of the chemistry of the multicomponent sol−gel reaction is often successful in realizing homogeneous multicomponent materials.[6]

Recently, we have reported the effect of various synthetic conditions on the production of homogeneous vanadia−silica xerogels, materials with recognized catalytic,[6] semiconducting, and photochemical properties.[7,2d,3] It was found that both the water content of the initial sol and the humidity under which aging of the gel was carried out dramatically affected the homogeneity of the final material. To isolate the effects of water and humidity, this study was carried out in the absence of any sort of added catalyst. Traditionally, however, the sol−gel synthesis of silica is usually catalyzed by Brønsted acids that accelerate the hydrolysis of the silicon esters used in the reaction.[8] Acid catalysis of silica sols, in the presence of transition metal ions, is likely to affect not only the silicon hydrolysis but also the solution chemistry of the particular metal. In the case of high-valent early transition metals, changes in pH are often accompanied by rapid changes in molecular complexity, and for some metals, the formation of high nuclearity molecular species is observed.[9] This suggests

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that pH may significantly affect the particular metal species ultimately incorporated into multicomponent system and, hence, influence bulk properties such as homogeneity. In fact, the need to control pH was noted previously in the production of homogeneous titania−silica glasses, where a very low pH, attained by the addition of strong mineral acids, is necessary to achieve homogeneous materials.[10] In the case of vanadia−silica xerogels, the use of acids such as HNO_3 and HCl to catalyze hydrolysis of the silica is common, and numerous investigations into the properties of materials made in this fashion have been carried out.[11,12] To the best of our knowledge, however, a systematic study of how acid catalysis affects the properties of vanadia−silica xerogels has not been previously performed. We report here the results of an investigation of the effects of HCl and HNO_3 on the properties of vanadia−silica xerogels.

Experimental Section

Reagents. Tetramethyl orthosilicate (TMOS; 99+%) and oxovanadium triisopropoxide were purchased from Gelest. TMOS was used as received, while oxovanadium triisopropoxide was vacuum distilled directly prior to use. All synthesis was carried out using deionized water (18.0 mho; Barnsted E-Pure system). 2-Propanol (99.5%, HPLC grade) was obtained from Aldrich and used as received. HCl and HNO_3 (concentrated, reagent grade) were acquired from Fisher and used as received.

Xerogel Synthesis. Sols were made by the slow addition of a water/2-propanol/acid mixture to an alcoholic solution of tetramethyl orthosilicate and the desired quantity of oxovanadium triisopropoxide. All solutions were ultrasonically mixed for a period of 5 min to ensure homogeneous mixing. After addition, 4 mL of the sol were placed in 1 cm styrene cuvettes, sealed, and allowed to gel. After gelation, the caps were removed and the cuvettes were placed in closed, humidity-controlled chambers for aging and evaporation. Humidity was maintained at 15% relative humidity (RH) by the use of saturated LiCl solutions. The saturated solutions were changed weekly to maintain a constant environment. Typical aging−evaporation times were on the order of 3 months. The samples were then dried in a programmable furnace. They were initially ramped to 100 °C at a rate of 5 °C/h, where they were allowed to dry for 72 h. They were then ramped at the same rate to 500 °C, where they were maintained for 36 h. Finally, they were cooled back to room temperature over a period of 95 h.

Thermal Analysis. The samples were analyzed using a TA Instruments Inc. Model 1600 differential thermal analyzer. The heating rate used was 10 °C/min from room temperature to 1400 °C. Samples were run under an air purge of 100 cm^3/min. Platinum sample pans were used for the analysis. The instrument was calibrated using a pure silver standard.

Raman Spectroscopy. Raman spectra of homogeneous xerogels were collected at 90° from the incident radiation, which passed through the center of the transparent monolithic sample, sealed in a 5 × 5 mm quartz fluorescence cell. Raman spectra of the heterogeneous samples were collected at 90° from incident irradiation impinging on powders sealed in a 6 mm quartz tube. All samples were baked out at 500 °C under an oxygen flow for 12 h in the sample holder and then closed off under oxygen just prior to measurement. Incident radiation was from the 514.53 nm (~1 W) line of a continuous wave argon ion laser (Coherent Innova-90). Inelastic scattering was collected through a 0.85 m *f*/7.8 double grating spectrometer, a modified Czerny-Turner operating in additive dispersion (Spex 1403) having 2400 groove/mm gratings, 102 × 102 mm, cosecant drive to allow linear frequency scanning. The laser line was filtered using a Spex 1460 Lasermate grating monochromator before entering the macrosampling chamber (Spex 1459 UVISIR Illuminator). Samples were mounted in an XYZ, micrometer-controlled translation stage. Detection was with a Burle C31034 11 stage GaAs photomultiplier (dark noise of 30−100 counts/second) contained in a thermoelectrically cooled housing (Products for Research) and operated in single photon counting mode using an external preamplifier−discriminator having <40 ns pulse-pair resolution and a digital photon counter (Spex DPC-2). The spectrometer and data acquisition and display were controlled by a computer program written in-house by Laser Laboratory personnel in the Microsoft FORTRAN and Microsoft Assembler programming languages and run on an IBM PC computer.

^{51}V NMR Spectroscopy. Solid-state vanadium-51 MAS NMR spectra were acquired using a 4.7 T IBM/Bruker WP200SY NMR spectrometer with solid-state accessory package. Spectra were obtained with the spectrometer frequency of 52.64 MHz, 50 kHz sweep width, 4 μs (90°) pulse, 1 s repetition delay, and no decoupling. The spectra were collected without spinning as static wide-line spectra. The samples were baked out at 500 °C in a 6 mm quartz tube under an oxygen flow for 12 h prior to measurement. After baking, the tube was evacuated and flame sealed. The sealed tube fit into the 7 mm stator of the Doty Scientific Inc. multinuclear probe. Typically, 10 000 scans were acquired. A vacuum-sealed sample of neat $VOCl_3$ was used as an external reference (0 ppm).

X-ray Diffraction. X-ray powder diffraction was collected on a Siemens D500 $\theta-2\theta$ diffractometer using Cu Kα radiation (30 mA at 40 kV). The instrument was configured with a diffracted beam monochromator, which was configured with 1.0° divergence slits, and 0.15° receiving slits.

Electron Spin Resonance Spectroscopy. Electron spin resonance spectroscopy (ESR) was performed on a Varian E-Line spectrometer operating in X band. Spectra were collected on solid powdered samples at 77 K. Anisotropic parallel and perpendicular **g** and **A** values were determined from the spectra.

Electronic Spectroscopy. Electronic spectra were recorded as transmission spectra on an On-Line Instruments Cary-14 conversion. Spectra were collected in transmission mode through ~5 mm xerogel flats. The aged but unprocessed gels were recorded under ambient conditions while the processed flats were baked out at 500 °C and sealed in a 5 × 5 mm quartz fluorescence cell through which the spectra were collected.

Results and Discussion

Multicomponent vanadia−silica xerogels were synthesized by the co-condensation of tetramethyl orthosilicate (TMOS) with oxovanadium triisopropoxide ($OV(O^iPr)_3$) in aqueous 2-propanol (eq 1).[3]

$$m\mathrm{Si(OMe)_4} + n(^{i}\mathrm{PrO})_3\mathrm{VO} + {}^{7}\!/_{2}(m+n)\mathrm{H_2O} \rightarrow [\mathrm{Si}_m\mathrm{V}_n\mathrm{O}_{(2m+2.5n)}] + 4m\mathrm{MeOH} + 3n^{i}\mathrm{PrOH} \quad (1)$$

When run under conditions of low water (3:1 H_2O:Si), homogeneous xerogels containing vanadium concentrations up to 1.5 mol % were obtained after low humidity aging (15% RH) and drying (500 °C).[6] At higher water or vanadium content, a heterogeneous green phase formed during the aging process, which resulted in heterogeneous orange xerogels after drying. Omitted from this earlier investigation was the use of an acid catalyst such as HCl, which is commonly used in the sol−gel synthesis of multicomponent materials includ-

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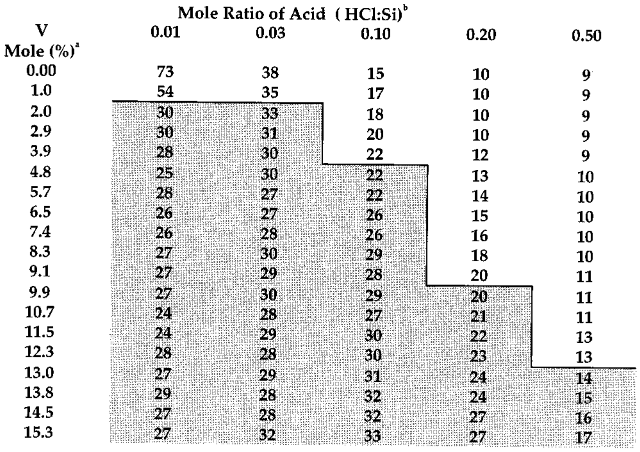
Table 1. Gelation Times (days) for HCl-Catalyzed Vanadia−Silica Sols[c]



V Mole (%)[a]	Mole Ratio of Acid (HCl:Si)[b]				
	0.01	0.03	0.10	0.20	0.50
0.00	73	38	15	10	9
1.0	54	35	17	10	9
2.0	30	33	18	10	9
2.9	30	31	20	10	9
3.9	28	30	22	12	9
4.8	25	30	22	13	10
5.7	28	27	22	14	10
6.5	26	27	26	15	10
7.4	26	28	26	16	10
8.3	27	30	29	18	10
9.1	27	29	28	20	11
9.9	27	30	29	20	11
10.7	24	28	27	21	11
11.5	24	29	30	22	13
12.3	28	28	30	23	13
13.0	27	29	31	24	14
13.8	29	28	32	24	15
14.5	27	28	32	27	16
15.3	27	32	33	27	17

[a] Mole percent = [V/(V + Si)] × 100. [b] [Si] = 2.05 M. [c] The shaded area denotes materials that were heterogeneous after aging.

ing vanadium−silicon xerogels and aerogels.[11,12] Because of its widespread use, it is important to understand the effect acids have on the distribution of the vanadium and the homogeneity of the final xerogel. To this end a series of sols was made with vanadium loadings ranging from 1 to 15.3 mol % vanadium (V/(Si + V) × 100). HCl was added to the sol in acid-to-silicon ratios (HCl:Si) of 0.01, 0.03, 0.10, 0.20, and 0.50:1 with the water-to-silicon ratio (H_2O:Si) held constant at 3:1.

Since HCl is added as a catalyst, it is worthwhile to note its effectiveness in inducing gelation in the presence of vanadium. The gelation times for all the sols are shown in Table 1. Consistent with many previous studies of acid catalysis of silica sol−gel systems, the gelation times for the pure silica control samples are strongly inhibited at the lowest acid concentration (0.01 HCl:Si; pH ~1.7), which is close to the point-of-zero-charge (pzc) of the silica (pH ~2). As more acid is added, the gelation times decrease significantly until, at the highest concentration, they are almost an order of magnitude faster.[13] In our previous study we reported that vanadium ions, even in low concentrations, strongly inhibited gelation. In the presence of acid, however, inhibition due to vanadium does not appear to be as significant. At 0.01 HCl:Si and at concentrations of vanadium above 1 mol %, the gelation time is approximately a factor of 3 faster than for sols containing no vanadium. Under these conditions, increasing the vanadium concentration above 1% results in only a modest decrease in gelation times. As the acid is increased, the effect of the vanadium becomes less pronounced and then, at the highest acid concentration, which corresponds to the quickest gelation times, some inhibition due to vanadium emerges and the gelation times appear to increase slightly. Notably, however, at the higher vanadium concentrations, the gelation times are relatively constant (within a factor of ~2), regardless of the acid concentration.

Qualitative effects of HCl on the homogeneity of the vanadia−silica sol−gel materials can be seen in Figure 1. All of the sols, regardless of vanadium or acid concentration, were homogeneous, transparent, and orange in color until past the gelation point. After aging for 4 weeks the gels began to take on a green color. The intensity of the green color increased both with increasing vanadium and with increasing acid concentrations. In a previous study we reported that vanadia−silica gels, made with no acid, formed a heterogeneous green phase at high vanadium concentrations.[6] This heterogeneous phase was determined to arise from partial reduction of self-condensed vanadia that formed in the pores of the silica matrix. The green gels that formed from under HCl catalysis, however, differ significantly from the previously characterized green heterogeneous gels in that, notwithstanding their color, they remain entirely homogeneous and transparent. As the materials continued to age, the color continued to transform until, at the end of 12 weeks, the gels had turned bright blue. In these blue materials evidence of heterogeneity, characterized by turbidity and eventual opacity, is obvious at vanadium loadings of 13.0 mol % and higher (Figure 1). The onset of heterogeneity as a function of the mole percent vanadium and the acid concentration is shown in the shaded area of Table 1. At 0.01 and 0.03 HCl:silicon ratios, vanadium concentrations above 1.0 mol % were heterogeneous. As the acid concentration increased, homogeneity was maintained at progressively higher vanadium concentrations. The highest concentration of vanadium we were able to incorporate and still retain homogeneity was 12.3 mol %, which was accomplished at a 0.5:1 HCl:Si concentration.

The electronic spectrum of an aged, blue xerogel containing 0.05 mol % vanadia:silica shows a broad, low-energy transition at $\lambda_{max} = 724$ nm (Figure 2a). The energy and intensity of this band is quite characteristic of V(IV) complexes, suggesting that the metal has been reduced during the sol−gel process.[14] Reduction is shown definitively by electron spin resonance (ESR) spectroscopy, which shows a spectrum characteristic of V(IV) ($I = {}^7/_2$, $S = {}^1/_2$) for the blue material (Figure 3).[15] Vanadium(V) is a reasonably strong oxidant under conditions of low pH ($E° = 1.00$ V), and in fact, HCl has long been known to react with V_2O_5 to produce chlorine gas and V(IV) ions.[16] It is therefore reasonable to conclude that HCl is acting both as an acid and as a reductant in this process. The particular vanadium(IV) species produced in the reduction is unknown, though reduction of V(V) oxides in an aqueous acid medium is likely to produce V(IV) vanadyl complexes: VO^{2+}.[16] This suggestion is supported by the ESR spectrum, which is anisotropic and can be interpreted in terms of axial symmetry with values of the parallel and perpendicular components of the **g** and **A** tensors calculated from the spectrum to be $g_{||} = 1.94$, $g_{\perp} = 2.01$ and $A_{||} = 80$ G and $A_{\perp} = 200$ G. These values are quite typical for discrete V(IV) vanadyl complexes such as $OV(H_2O)_5{}^{2+}$ and of

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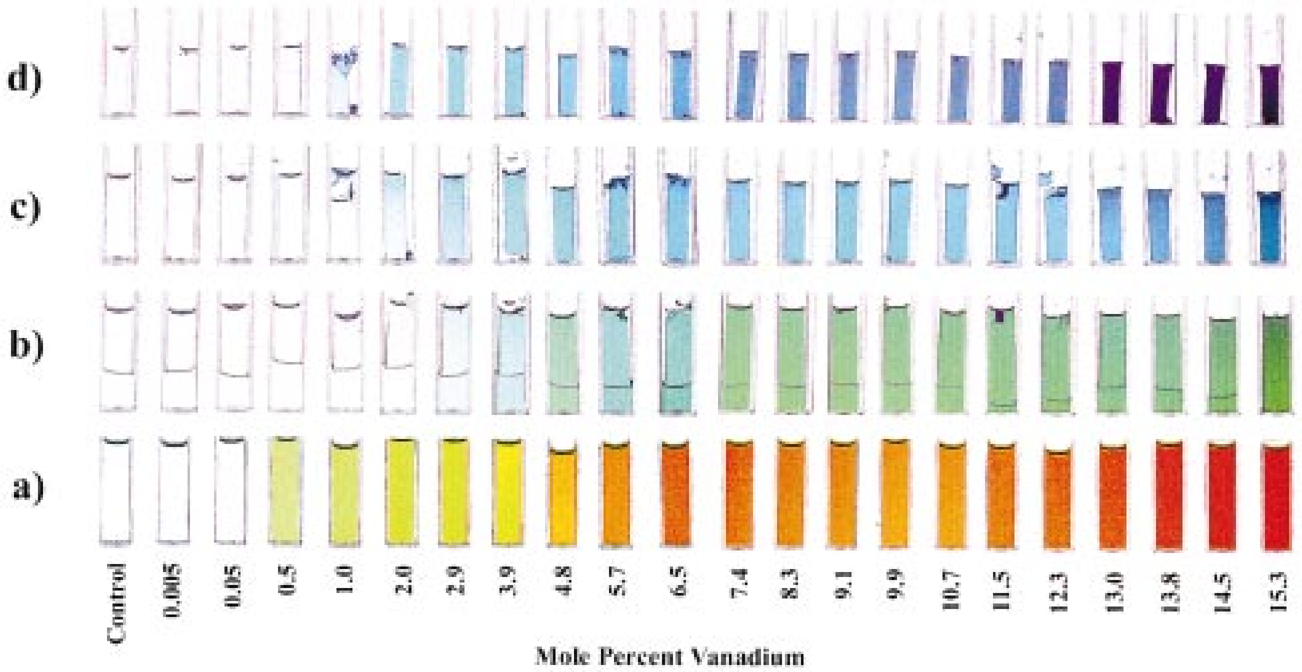

Figure 1. Vanadia−silica gels of varying vanadium concentration made with 0.5:1 HCl:Si at (a) 1 week, (b) 4 weeks, (c) 8 weeks and, (d) well after aging is complete (36 weeks).

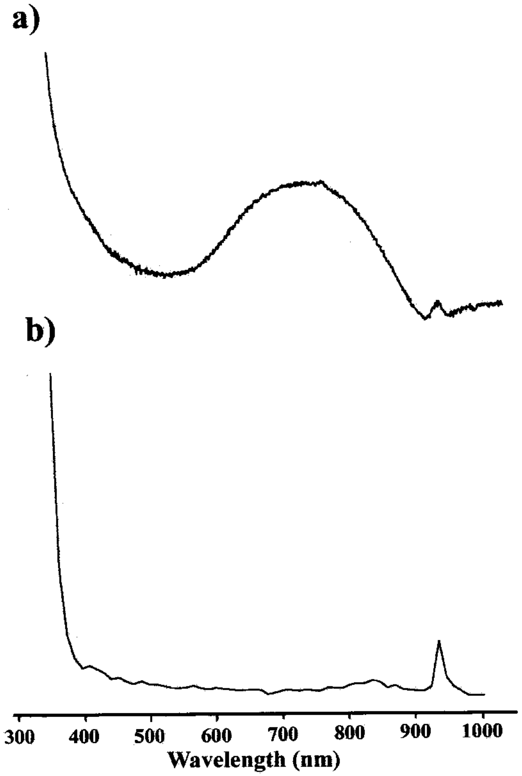

Figure 2. Electronic spectra of (a) blue unprocessed xerogel and (b) 500 °C processed xerogel containing 0.05 mol % V made at 0.20:1 HCl:Si.

V(IV) vanadyl complexes dispersed on substrates such as alumina and silica.[17]

At the conclusion of aging, the xerogels were taken slowly to 500 °C over a period of 36 h. After drying, the blue color was gone and the resulting xerogels ranged from colorless to dark orange, depending on their vanadium concentration. Significantly, the demarcation between homogeneous and heterogeneous materials seen in the blue aged xerogels is retained in the dried xerogel (though the dried materials become orange). Materials made at 0.5:1 acid were transparent up to 12.3 mol %, while those containing 13.0 mol % and above were quite obviously opaque. After thermal processing, the physical integrity of the xerogel monoliths decreased with increasing vanadium content. Processed xerogels up to 4.8 mol % remained as solid, relatively crack-free monoliths. From 5.7 to 9.9 mol % they remained intact, but all were significantly cracked. At loadings close to the limit of homogeneity (12.3 mol %), the monoliths did not maintain their integrity, though fairly large transparent fragments could be retrieved for spectroscopic analysis. The heterogeneous materials, 13.0 mol % and above, were all powders after thermal processing.

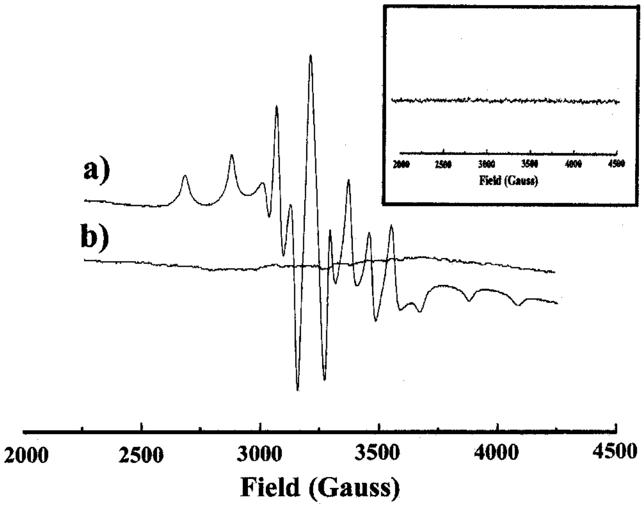

Figure 3. Electronic spin resonance spectra of (a) blue unprocessed xerogel, (b) 500 °C processed xerogel, and (inset) 125 °C processed xerogel containing 4.8 mol % V (0.20:1 HCl:Si).

The processed xerogels were ESR silent (Figure 3), which, in conjunction with the disappearance of the 724

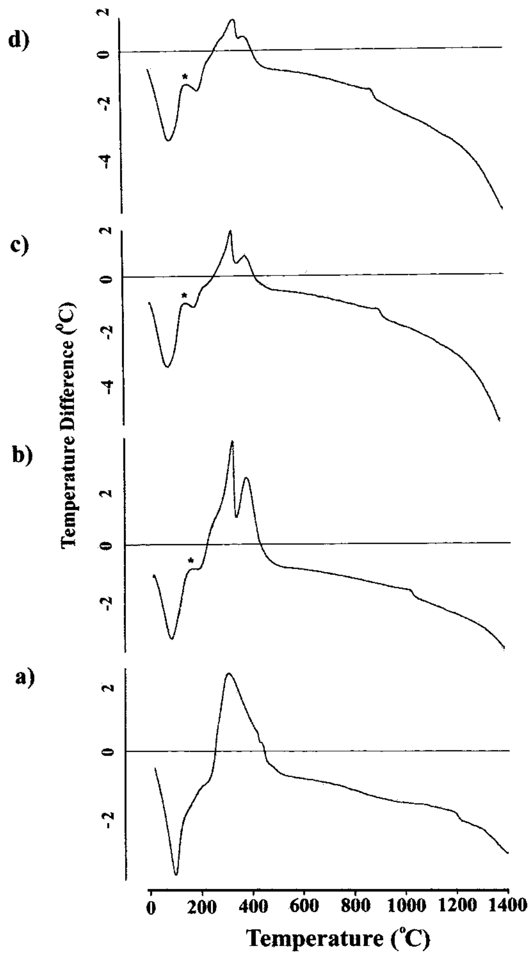

Figure 4. Differential thermal analysis of (a) pure silica and gels with (b) 4.8 mol %, (c) 7.4 mol %, and (d) 9.1 mol % V (0.20:1 HCl:Si; * indicates vanadium concentration dependent exotherm at 176 °C).

nm band in the electronic spectrum (Figure 2b), indicates that they have been reoxidized to V(V). It is of some interest to understand at what temperature this oxidation occurs and, further, to understand the effect the vanadium has on the complete drying and densification of the xerogel. To this end, thermal analysis of the drying process, as a function of vanadium concentration, was carried out by differential thermal analysis (DTA). The DTA trace (Figure 4) of a pure silica control sample, run at 10 °C/min under a flow of dry air, shows a sharp endotherm at 102 °C, which is associated with desorption of water and alcohol trapped in the pores of the xerogel. At 325 °C a strong exotherm appears, which is due to the oxidation of organic material left in the xerogel (i.e. unreacted alkoxide groups).[18] After this oxidation process, no significant features appear in the thermal trace until a small exotherm is recorded on the endothermic background at 1160 °C, directly before melting occurs at ~1300 °C. DTA traces of the vanadia–silica xerogels (Figure 4) show the same initial endotherm at 102 °C, followed by an exothermic region centered around 400 °C. There are notable differences, however, between the pure silica and the vanadia–silica xerogels in the exothermic region. The most obvious difference is the resolution of two sharp peaks, which suggests two distinct exothermic processes at 375 and 415 °C. While the presence or, possibly, the resolution of these peaks is clearly dependent on the presence of vanadium, their heights do not appear to scale in any direct fashion with vanadium concentration. In fact, the peaks are sharper and more distinct at the lowest vanadium concentration. This would seem to be inconsistent with a thermal process that involves oxidation of the vanadium site. In addition to the two exotherms at 375 and 415 °C, another exotherm appears at 176 °C, directly after and slightly overlapping the solvent evaporation endotherm. Unlike the higher temperature exotherms, the one at 176 °C increases with increasing vanadium concentration. To ascertain which, if any, of these exothermic processes involves oxidation of vanadium, five xerogels (0.5 mol % V) were placed in a tube furnace under an O_2 flow and dried for 12 h, respectively, at 95, 125, 175, 350, and 435 °C. After heating, the sample that was heated to 95 °C, which is close to the bottom of the water/alcohol desorption endotherm, remained blue and had an ESR spectrum that was unchanged from that of the aged, unheated materials. The xerogels heated to 125 °C, which lies on the low-temperature side of the 176 °C vanadium-dependent exotherm, had lost its blue color and was ESR silent (Figure 3, inset), verifying that reoxidation had occurred. As would be expected, all xerogels processed at temperatures higher than 125 °C were also fully oxidized. Clearly, reoxidation occurs at a relatively low temperature and it seems likely that the 176 °C exotherm corresponds to this process. However, since reoxidation is actually observed at temperatures below the 176 °C exotherm (i.e. 125 °C), we cannot fully rule out the possibility that the V(IV) reoxidation exotherm actually occurs at lower temperature and is obscured in the DTA by the large, low-temperature solvent desorption endotherm.

Apart from the assignment of the V(IV) oxidation exotherm, there are several other trends observable in the DTA traces that depend on the vanadium concentration. The small exotherm that takes place before melting has been observed previously in acid-catalyzed silica xerogels. It is irreversible and has been ascribed to structural relaxation of the matrix that is accompanied by some skeletal densification.[19] This assessment is consistent with the relatively abrupt changes observed in the density, surface area, porosity, and morphology at temperatures in the range of this exotherm.[20] As can be seen in Figure 4, this exotherm is also observed in the vanadia–silica xerogels, where it occurs at progressively lower temperatures as the vanadium concentration increases. Specifically, at 4.8, 7.4, and 9.1 mol % vanadia, it occurs at 1040, 930, and 885 °C, respectively. The melting point also decreases with increasing metal concentration, but the effect is less pronounced. It is likely that the origin of these trends lies in the introduction of V–O–Si and V–O–V linkages into the silica matrix. These are weaker bonds and, hence, more thermally labile. The effect is probably analogous in some respects to the reduction in viscosity

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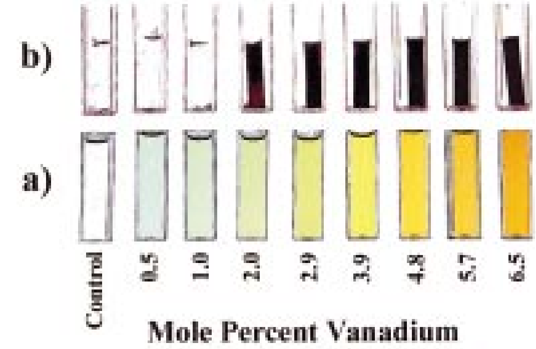

Figure 5. Vanadia−silica gels of varying vanadium concentrations made with 0.10:1 HNO_3:Si at (a) 1 week and (b) 3 months.

of silica glasses that occurs when alkali and alkaline earth ions are added.[21]

A notable aspect of the HCl-catalyzed synthesis of multicomponent vanadia−silica xerogels is the high loadings of vanadium that can apparently be realized while the homogeneity is still maintained. At the highest acid concentration, xerogels containing 12.3 mol % vanadium are highly transparent. The high concentrations that can be attained under these conditions most likely arise from differences in reactivity between V(IV) and V(V). When the vanadium remains in the V oxidation state, hydrolysis and condensation rates are rapid, and self-condensation is favored. Excessive self-condensation ultimately leads to vanadia rich areas that ultimately phase separate. In the lower oxidation state, the rates of hydrolysis and condensation are much slower and more closely match the rates of those processes for the silicon alkoxide.[9] This ultimately favors a more homogeneous dispersion of the metal through the silica. This argument implies that it is the reductive properties of HCl and not its acidity that yields an increase in homogeneous vanadium loadings.

This supposition was tested by using a nonreducing acid, in particular, HNO_3. Using conditions identical to those employed in making the HCl-catalyzed materials, a series of sols were made with vanadium concentrations from 0.5 to 6.5 mol % (V/(V + Si)). The qualitative evolution of these materials during the aging process is shown in Figure 5. Directly after preparation and up through the gelation point, the sols were orange in color and homogeneous over the whole range of metal concentrations. After gelation, the higher vanadium loadings began to turn green. Unlike the HCl-catalyzed materials, this green color was in all cases accompanied by heterogeneity. As mentioned, a green heterogeneous phase is observed under conditions of high water or vanadium when no acid was employed. This phase was identified as being a partially reduced (mixed valence) vanadia gel, which formed in the silica matrix. The heterogeneous green phase present in the HNO_3-catalyzed materials proved to be identical.[22] In general, the use of a strong but nonreducing acid such as HNO_3 results in a homogeneous concentration range very close to that found with no added catalyst. In short, the acidity appears to provide no significant increase in homogeneous vanadium concentration. These results provide strong support for the contention that the increased homogeneity observed with HCl catalysis results primarily from the reduction process.

The loss of transparency and the visual observation of opaque regions in the xerogels qualitatively define the onset of heterogeneity. This onset occurs rather abruptly (Figure 1) between 12.3 and 13.0 mol %. This is, of course, a purely qualitative observation. It is therefore important to quantify both the onset of heterogeneity and the nature of the heterogeneous phases. In vanadia−silica glasses made with low vanadium content, the vanadium is dispersed as discrete, monomeric sites, bonded to the silica by V−O−Si linkages. As the concentration of vanadium increases, more V−O−V linkages occur as more dimeric and oligomeric vanadia species form. It is possible that, regardless of the vanadium content, the materials will remain optically transparent as long as they remain amorphous. Heterogeneity, at least in the optical sense, originates from scattering sites in the material whose dimensions are close to the wavelength of the incident radiation. In materials such as these, a likely origin of those sites is from phase-separated crystalline metal oxide regions.

The X-ray diffraction (XRD) pattern of dried, vanadia−silica xerogels from 12.3 to 15.3 mol % V is shown in Figure 6. Consistent with the qualitative observation of homogeneity in the 12.3 mol % material, the XRD shows a broad amorphous background, characteristic of amorphous silica, at $2\theta = 23.5°$ with no diffraction pattern indicative of a crystalline phase observed. Xerogels containing 15.3 mol % V, which are very heterogeneous, show strong diffraction from crystalline phases in the XRD, suggesting that, at least in part, this is the origin of the heterogeneity. The observed diffraction pattern, with reflections at 2θ values of 20.3°, 21.7°, 26.1°, and 31.0°, establishes V_2O_5 as the predominant crystalline phase.[23] At 13.0 mol % V, the first visual evidence of heterogeneity is observed; however, the XRD of that material shows no distinct diffraction pattern that can be observed above the amorphous background. In fact, an unambiguous diffraction pattern is not observed until 13.8 mol % V is reached. It appears that, for these materials, the XRD measurement provides valuable information about the nature of the crystalline heterogeneous phase but does not appear to significantly elucidate the transition from homogeneity to heterogeneity beyond that of visual observation.[24]

In vanadia−silica xerogels made from V(V) complexes, the vanadium oxide center is dispersed as a pseudotetrahedral site with a short terminal vanadium oxygen bond and three basal-plane V−O−Si linkages connecting the vanadium into the silica network.[3,11] One question that can be raised is whether the V(V) center that results from reoxidation of the V(IV) also has that

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[22] In our previous report (ref 6) the green heterogeneous phase that forms under conditions of high water and/or vanadium content in the uncatalyzed vanadia−silica xerogels was identified, on the basis of a characteristic near-IR ($\lambda_{max} = 1430$ nm) and ESR spectra ($g_{\parallel} = 1.935$, $g_{\perp} = 1.993$, $A_{\parallel} = 199$ G, and $A_{\perp} = 68$ G), as being identical to partially reduced pure vanadia gels which had been previously investigated (Babonneau, F.; Barboux, P.; Josien, F. A.; Livage, J. *J. Chim. Phys.* **1985**, *82*, 761 and Araki, B.; Audiéres, J. P.; Michaud, M.; Livage, J. *Bull. Soc. Chim. Fr.* **1981**, *9−10*, 366.). Identical near-IR and ESR were obtained for the heterogeneous green phase that formed under nitric acid catalysis.

[23] Enjalbert, R.; Galy, J. *Acta Crystallogr. C* **1986**, *42*, 1467.

[24] We cannot, of course, rule out scattering sites that are amorphous yet accumulate in regions that are heterogeneously distinct from the silica matrix and are large enough to scatter light.

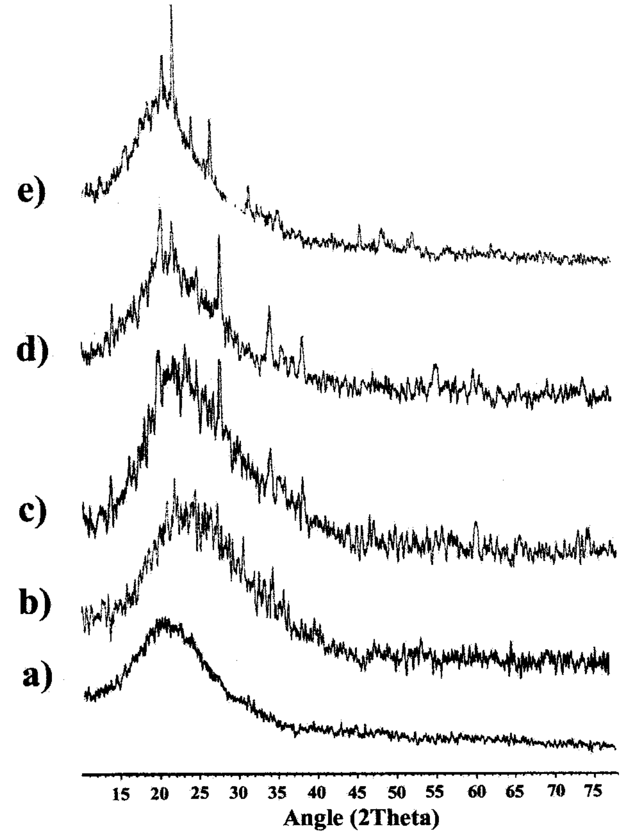

Figure 6. X-ray diffraction patterns of processed (500 °C) xerogels containing (a) 12.3 mol %, (b) 13.0 mol %, (c) 13.8 mol %, (d) 14.5 mol %, and (e) 15.3 mol % V (0.50:1 HCl:Si).

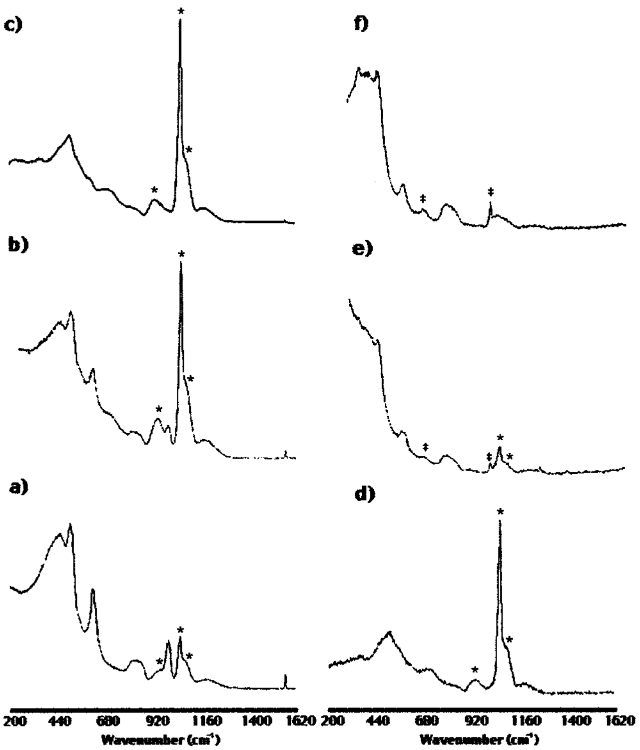

Figure 7. Raman spectra of processed (500 °C) xerogels containing (a) 1.0, (b) 4.8, (c) 9.1, (d) 12.3, (e) 13.0, and (f) 15.3 mol % V (0.50:1 HCl:Si) (* corresponds to pseudotetrahedral oxovanadium and ‡ to crystalline V_2O_5).

pseudotetrahedral geometry. Pseudotetrahedral oxovanadium sites have been characterized by a variety of techniques, including vibrational spectroscopy (Raman and FT-IR) and solid state ^{51}V NMR.[25–27] Raman spectra of homogeneous and discretely dispersed vanadia–silica xerogels show a strong sharp peak at 1038 cm^{-1}, which has been assigned to a vibration that is predominantly the terminal V=O stretch.[25] A weaker band, associated with the V–O–Si stretch, occurs at ~970 cm^{-1}, and finally, there is a band at 1080 cm^{-1}, which appears as a shoulder on the 1038 cm^{-1} V=O stretch.[11b,28] Figure 7 shows Raman spectra for the series of vanadia–silica xerogels from 1 to 14.5 mol % V, made at a 0.5:1 HCl:Si ratio. The spectrum of the 1.0 mol % vanadium xerogel clearly indicates that pseudotetrahedral geometry has been realized upon reoxidation. The spectrum shows all the characteristic peaks, including the strong terminal V=O stretch at 1038 cm^{-1}, the shoulder at 1080 cm^{-1}, and the bridging stretch at 970 cm^{-1}. As the concentration of vanadium is increases, the 1038 cm^{-1} terminal stretch becomes much stronger but does not change position or band shape, which is consistent with a continuous increase in pseudotetrahedral sites and is inconsistent with the formation of other vanadia phases. The band at 970 cm^{-1} is partially occluded by the intrinsic Si–OH stretch in the silica xerogel, which occurs at 977 cm^{-1} and, therefore, appears as a shoulder in the 1 mol % vanadium sample. At 4.8 mol % the transition is no longer a shoulder but is resolved into a distinct peak centered around 920 cm^{-1}. As the vanadium concentration continues to increase, the band grows more intense and shifts to lower energy until, at 12.3 mol %, it is a broad well-resolved peak at 914 cm^{-1}. At 13.0 mol % vanadium, which corresponds to the onset of heterogeneity, the spectrum changes dramatically. The V=O stretch at 1038 cm^{-1} is present, albeit considerably weaker than in any of the homogeneous materials. More importantly, the spectrum shows several new bands not found in the spectra of the homogeneous material. A sharp peak is observed at 996 cm^{-1} with a weaker peak appearing at 696 cm^{-1}. Consistent with the observation of V_2O_5 in the XRD, these Raman peaks correspond to the A_g (V=O) and B_{2g} modes of crystalline vanadium oxide.[29] At 15.3 mol % vanadium these peaks become more intense while the 1038 cm^{-1} band, associated with the pseudotetrahedral V=O group, is almost completely gone. In general, the Raman spectra support the conclusion drawn from qualitative visual observation that there is a relatively abrupt transition from homogeneous to heterogeneous when the concentration goes from 12.3 to 13.0 mol %. At 13.0 mol % the Raman spectrum clearly shows that phase-separated crystalline V_2O_5 and dispersed pseudotetrahedral VO_4 groups coexist. At 15.3 mol % vanadium, the materials are exceedingly hetero-

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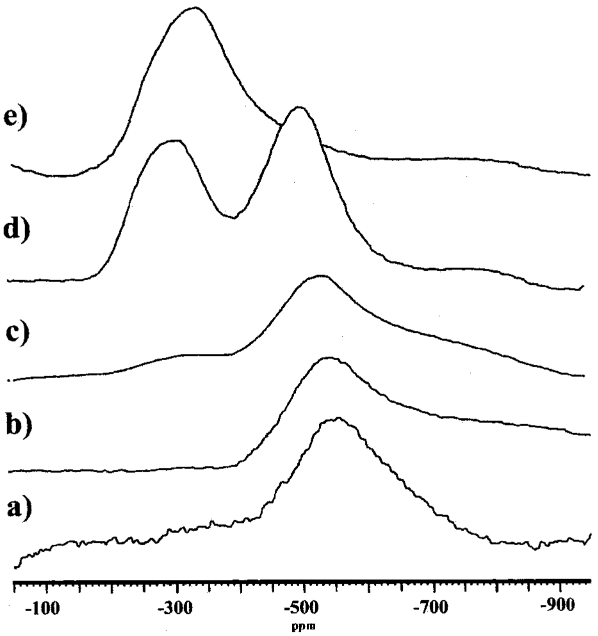

Figure 8. ^{51}V wide-line solid-state NMR spectra of processed (500 °C) xerogels containing (a) 0.5 mol %, (b) 4.8 mol %, (c) 12.3 mol %, and (d) 15.3 mol % V (0.50:1 HCl:Si) and (e) ^{51}V wide-line solid-state NMR spectra of pure V_2O_5.

geneous and the Raman spectrum indicates that V_2O_5 is the dominant phase.

Similar evidence supporting the limits of homogeneity of HCl prepared vanadia−silica xerogels is obtained from ^{51}V NMR spectroscopy. Figure 8 shows the static spectra for a series of vanadium loadings. The very dilute xerogels containing 0.5 mol % vanadium show an anisotropic resonance whose most intense line shape component is at −550 ppm (relative to $VOCl_3$) in the ^{51}V NMR. Previous studies have shown that this resonance is consistent with discrete pseudotetrahedral VO_4 sites.[27] As the concentration increases, this peak remains relatively unchanged in position but becomes more intense. At 12.3 mol % vanadium, which is the limit of observed homogeneity, the ^{51}V NMR shows, in addition to the −550 ppm resonance, a weak resonance at −300 ppm appears. The −300 ppm feature gains dramatically in intensity in going to very heterogeneous 15.3 mol % materials. ^{51}V NMR resonances in this range correspond to vanadium with higher coordination numbers.[28] In particular, this peak agrees well with that of a known sample of V_2O_5, though other highly associated vanadia species may also be present. The assignment of this band to V_2O_5 is, of course, consistent with the Raman and X-ray determination. Regardless, the −300 ppm resonance appears to correlate well with the onset of heterogeneity in the sample. What is particularly interesting about the NMR result is that it shows the presence of small amounts of heterogeneous phase, even in material that is qualitatively homogeneous. While the heterogeneous phase at this concentration was not detectable by the other methods, it represents a more reasonable physical picture wherein the transition between homo- and heterogeneous xerogels involves the formation of very small, possibly nanocrystalline, phase-separated regions at vanadium loadings just below the visibly noticeable onset of heterogeneity.

There are a number of conclusions that can be drawn from this study. Principal among these is that reduction of the metal to a lower oxidation state yields a dramatic increase in the amount of vanadium than can be incorporated while still retaining homogeneity. The materials produced by this means are homogeneous up to 12.3 mol % V (17 wt % V_2O_5), which is significantly higher in vanadium content than any previous reports of which we are aware. For example, Baiker et. al. have made extensive use of the sol−gel process to make multicomponent metal−silica materials for use as heterogeneous catalysts. For vanadia silica xerogels, made from mixing prehydrolyzed silica and vanadia sols, they report that at 10 wt % V_2O_5 crystalline phases are detected.[11a] Similarly, Wachs prepared vanadia−silica xerogels by a two-step process involving prehydrolysis of the silica with dilute nitric acid followed by the addition of oxovanadium triisopropoxide. In these materials a crystalline phase is observed at both 1 and 3 wt % V_2O_5.[12] Since reoxidation yields the desired pseudotetrahedral oxovanadium species, this represents a useful synthetic approach to significantly increasing the vanadium loading. Whether this approach will also be viable for making other multicomponent metal−silica xerogels depends largely on the ability to reduce the metal and to recover the desired active site upon reoxidation. The reduction of V(V) to V(IV) has, of course, been used rather extensively to make supported heterogeneous catalysts by the wet impregnation technique. This process usually involves reduction of V(V) metavanadate to V(IV) with aqueous oxalic acid. The reduced solution is then slurried with the silica gel substrate, the solvent is removed, and the material calcined to reoxidize it to V(V). As in the case of the vanadia−silica xerogels, this reoxidation process generates the desired pseudotetrahedral V(V) sites. It is unclear, however, whether this technique yields more discrete dispersal of the metal sites over the substrate than can be obtained using V(V) reagents.

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