Vanadia−Silica Sol−Gel Derived Glass: Factors Affecting Homogeneity and Morphology

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The chemical and processing conditions under which multicomponent vanadia−silica sol−gel derived glass is synthesized have been investigated to determine the factors leading to homogeneity in the final material. In conjunction, studies were also conducted to assess changes in the morphological properties (porosity) of the silica xerogel due to the presence of vanadium. 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. High initial water content or high humidity aging conditions resulted in the formation of green gels containing partially reduced vanadia, which, upon drying at 500 °C, yielded opaque orange xerogels. Vanadia−silica gels made with low water and aged at low humidity remained transparent after drying. The amount of vanadium that could be incorporated while still maintaining homogeneity was increased significantly if low water and low humidity conditions were used in the process. The presence of the vanadium, even in low concentrations, dramatically affected the pore structure of the resultant xerogel. Materials with vanadium concentrations as low as 0.01 mol % were found to be significantly more microporous than pure silica control samples. Imaging by atomic force microscopy revealed that the increased microporosity was due to filling of the mesopore regions in the materials containing vanadium.

Introduction

The sol−gel preparation of multicomponent vanadia−silica glasses has been a subject of considerable recent interest. Investigations into this process have been driven, in large part, by the desire to prepare highly dispersed vanadia−silica heterogeneous catalysts.[1] To that end, a number of excellent studies of this system have been carried out that relate the morphology of sol−gel derived xerogels or aerogels and the distribution of vanadium sites in them to catalytic activity.[2−7] More recently, the ability of the sol−gel process to yield optically transparent materials has been exploited to produce vanadia−silica glasses for optical applications such as chemical sensing.[8] Taken together, these previous studies suggest that the sol−gel process, in the presence of vanadium ions, is relatively complex. The specific vanadium oxide species distributed in the silica matrix is influenced by the particular conditions of the sol−gel reaction. In turn, the metal can affect the sol−gel reaction and, as a result, the properties of the resultant xerogel. For all of the desired applications, however, the ability to systematically control the distribution of the vanadium sites, the homogeneity of the glass and its bulk morphological properties is of critical importance if desired properties are to be optimized.

Multicomponent vanadia−silica xerogels can be synthesized by the cocondensation of tetramethyl orthosilicate (TMOS) with oxovanadium triisopropoxide ($OV(O^iPr)_3$) in aqueous 2-propanol (reaction 1).[8]

$$m\,Si(OMe)_4 + n(^iPrO)_3VO + {}^7/_2(m+n)H_2O \rightarrow [Si_mV_nO_{(2m+2.5n)}] + 4m\,MeOH + 3n\,^iPrOH \quad (1)$$

Previously, this approach was used to produce homogeneous, optically transparent vanadia−silica xerogel monoliths containing up to 0.5 mol % vanadium (V/V+Si). Under the reaction conditions used, it was found that vanadium concentrations higher than 0.5 mol % yielded highly colored, opaque heterogeneous materials.[8] This limit depended both on the synthetic conditions under which the sol−gel reaction was run and on the conditions under which the gel was aged and dried. To fully understand these factors, with the ultimate goal of increasing the vanadium concentration while still retaining optical homogeneity, we have systematically varied specific reaction conditions and observed the effects on the properties of the xerogel. In particular, we have investigated how the water content and vanadium concentration of the initial sol and the humidity under which aging of the gel takes place affect the final material. We report here the results of that

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study. Other important influences such as pH and prehydrolysis of the silica will be reported at a later date, as will studies which elucidate the coordination environment and electronic structure of the vanadium centers.

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 (10^{-18} Ω; Barnsted E-Pure system).

Xerogel Synthesis. Sols were made by the slow addition of a water/2-propanol mixture to an alcoholic solution of tetramethyl orthosilicate and the desired quantity of oxovanadium triisopropoxide. After addition, 4 mL of the sol was placed in 1 cm styrene cuvettes, sealed, and allowed to gel. For studies of the water dependence of the reaction, solutions containing 0.5 mol % vanadium and control samples containing no vanadium in 2-propanol were made with varying water-to-silicon ratios. The silicon concentration was held constant in all of the sols, and the desired water-to-silicon ratios were attained by reducing the amount of 2-propanol solvent. 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% and 47% relative humidity by the use of saturated LiCl and KSCN solutions, respectively.[9] The saturated solutions were changed weekly to maintain a constant environment. The evolution of the aging−evaporation process was monitored by recording the weight loss of the samples. When weight loss became insignificant ($\Delta m \leq 0.003$ g/week) the xerogels were judged to be at equilibrium and the aging process was deemed to be completed. Typical aging−evaporation times were on the order of 4 months for gels at 15% relative humidity and as long as 10 months for gels aged at 47% relative humidity. The actual time depended on the initial water content of the sample. The samples were then dried in a programmable furnace. Initially they were ramped to 100 °C at a rate of 5 °C/h, where they were allowed to dry for 72 h. The samples 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. After removal from the furnace they were stored in an inert atmosphere drybox.

Viscometry. Viscometry measurements were performed on a Brookfield DV-II+ rotating spindle viscometer equipped with concentric cylinder small-sample holder to obtain absolute viscosities. All measurements were collected at a shear rate of 3 s^{-1}. The sample was held at a constant 25 °C by means of a thermostated water jacket.

Gas Physisorption Measurements. Nitrogen adsorption−desorption measurements were performed at 77 K on a Micromertics ASAP 2010 sorptometer. Prior to measurement, all samples, previously dried at 500 °C, were degassed for 12 h at 150 °C. Adsorption and desorption isotherms over a range of relative pressures ($P/P°$) from 0.01 to 0.95 were collected for all samples.[10] Surface areas were determined from the Brunauer−Emmett−Teller (BET) equation in a relative pressure range between 0.01 and 0.10.[11] Pore volumes and pore size distributions were determined over the whole isotherm from density functional theory using a slit-pore model.[12] Micropore surface areas were estimated from t-plot analysis in the range $0.30 < t < 0.50$ nm using the Harkins−Jura correlation.[13,14] All isotherms are described using IUPAC nomenclature.[15]

Atomic Force Microscopy. Atomic force micrographs were measured on a Digital Instruments Dimensions 3000 scanning probe microscope. Images were collected in Tapping Mode on the interior of a freshly cleaved xerogel monolith using etched silicon tips. To eliminate the possibility that features observed in the AFM scan were artifacts, images were collected from multiple samples that came from different batches of each type of xerogel. In all cases the features observed in each type of sample (pure silica and 0.5% vanadium−silicon) were entirely reproducible; hence, the topological differences between them were judged to be real.

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

Electronic Spectroscopy. UV−visible-NIR spectra were collected as diffuse reflectance spectra on a Perkin-Elmer Lambda 19 equipped with a Labsphere RSA-PE−19 sphere accessory. Powdered samples were placed in a powder cell with black backing and a quartz window at an approximate thickness of 5 mm. The reference was an identical cell containing a NIST-traceable calibrated Spectralon standard.

NMR Spectroscopy. Solid-state ^{29}Si NMR spectra were recorded on a Brüker WP200SY NMR spectrometer with a solid-state accessory package. A Doty Scientific multinuclear CPMAS probe was employed to observe silicon-29 at 39.7 MHz. The magic angle and magnet homogeneity were optimized in the CPMAS carbon-13 mode by observing a *p*-di-*tert*-butylbenzene-packed zirconia rotor spun on the order of 4 kHz. For the MAS silicon spectra, recycle delays of 90 s were used after a 90° pulse to the observation channel. High-power proton decoupling was employed. Overnight runs were necessary to obtain satisfactory signal-to-noise ratios. Spectra were externally referenced to tetramethylsilane (TMS).

Results and Discussion

Gelation Kinetics. The kinetics of gelation for vanadia−silica and pure silica samples was monitored by the temporal changes in viscosity of the sols. In these measurements, the viscosity was determined at a constant shear rate of 3 s^{-1}, and the gelation time was assigned as the point where the viscosity exceeded the range of the instrument. Even small amounts of vanadium had a dramatic effect on the gelation time of the sol. Figure 1a shows the viscosity over time of a pure silica control and a 0.5% vanadium−silicon sol made with a 3:1 water-to-silicon ratio. The gelation time for the control was 104 h. That of the 0.5% vanadium sample was 605 h, an increase of almost 6-fold. Both the gelation times and the relative contours of the viscosity vs time plots for the two samples were different. Figure 1b shows the viscosity for the two samples vs a relative time (t/t'). The reference time (t') was taken as the time each sol took to attain a viscosity of 800 cP. The pure silica sample maintains a relatively low, constant viscosity until shortly before gelation, at which point it undergoes a sharp, rapid increase. Conversely, the sample containing 0.5% vanadium showed a gradual increase in viscosity, commencing at $t/t' \sim 0.75$, which continued until the gelation point was attained. This viscosity behavior suggests that the

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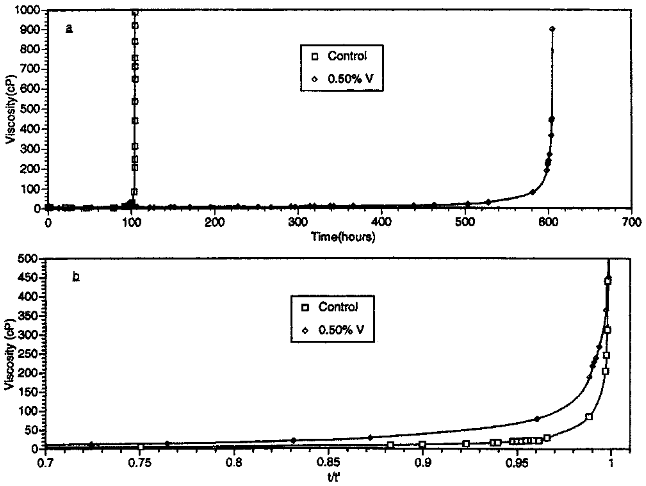

Figure 1. (a) Plots of viscosity vs time of a pure silica control and a 0.5 mol % vanadium−silicon sol made with 3:1 water-to-silicon ratio. (b) Plots of viscosity versus relative time (*t*/*t*′) of a pure silica control and a 0.5 mol % vanadium−silicon sol made with a 3:1 water-to-silicon ratio.

control sample undergoes a rather rapid transition from small, dilute silicate species to the contiguous polymer which constitutes the gelled material. The gradual increase in viscosity in the materials containing vanadium, however, suggests the slow formation of polysilicate agglomerates and micro gel particles which ultimately cross-link with each other to the point where gelation is attained. Similar differences in temporal viscosity profiles have been observed previously for acid vs base-catalyzed sol−gel reactions with similar assessments made about the origin.[16,17] As pointed out by Sacks and Sheu, no detailed growth pathways can be proposed from rheology data alone, as information about the specific molecular silicate species present is lacking.[16] Increases in the vanadium content resulted in a concomitant increase in gelation times until a mole ratio of ∼1% was reached. Above that ratio the gelation times began to decrease somewhat (gelation time for 1% V at 3:1 water was 503 h). In all cases, however, the materials containing vanadium gelled considerably slower than the corresponding control samples. Significantly, samples with a vanadium content as low as 0.05% (1.03 mM) were observed to inhibit gelation by a factor of 5 (3:1 water-to-silicon ratio).

The effect of increasing water concentration on the gelation times for silica sol−gel materials has been reported extensively for uncatalyzed, acid-catalyzed, base-catalyzed, and sequential acid−base-catalyzed gels.[16−20] In general, an increase in the water-to-silicon ratio results in a decrease in the gelation time. In keeping with these previous observations, our uncatalyzed control materials showed gelation times of 104, 25, and 4.25 h for water-to-silicon ratios of 3, 6, and 11 to 1, respectively. These values are consistent with times reported by Debsikdar for analogous sols.[21] For materials containing 0.5% vanadium a similar trend was observed with gelation times of 605, 208, and 193 h with water-to-silicon ratios of 3, 6, and 11 to 1, respectively. For all water concentrations, however, the presence of the vanadium strongly inhibited gelation.

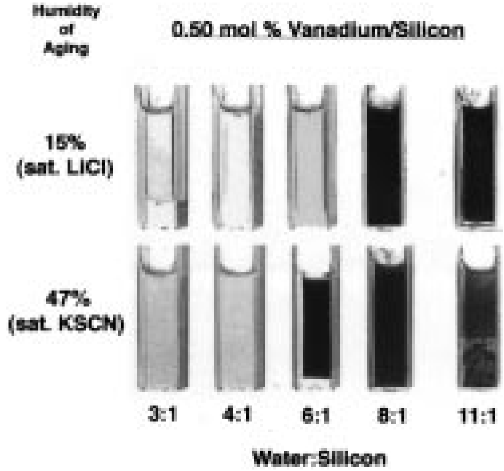

Figure 2. Gels of 0.5 mol % vanadium−silicon, made with varying water-to-silicon ratios and aged at two different humidities, approximately one-quarter of the way through the aging−evaporation process.

This inhibition also appears to be present in vanadia−silica sols made through prehydrolysis with sequential acid−base catalysis. As noted by Dutoit et al., as the vanadium content increases, more base is required to induce gelation.[6] The existence of this strong inhibition is somewhat surprising; the mechanism by which it occurs remains unclear. Other early high-valent transition metals, such as Ti(IV), have been reported to be sol−gel catalysts.[22] In the case of vanadium, we have previously found that oxovanadium triisopropoxide is an active catalyst for the transesterification of tetramethyl and tetraethyl orthosilicate with primary and secondary alcohols.[23] In addition, preliminary studies have shown it to be an efficient catalyst for the hydrolysis of orthosilicates in the early stages of the sol−gel process.[24] The inhibition, therefore, must stem from specific interactions of the metal with the silica during condensation or possibly from secondary effects of the metal on the chemistry (e.g. variations in pH). The fact that the inhibition is pronounced even at relatively low vanadium concentrations suggests that the metal may be acting catalytically.

Water and Vanadium Concentration Effects. Solutions containing 0.5 mol % vanadium and pure silica control samples were made with varying water-to-silicon ratios in 2-propanol solvent. The silicon concentration was held constant in all of the sols and the desired water-to-silicon ratios were attained by reducing the amount of 2-propanol. After gelation, all of the samples, regardless of water content, were orange in color, transparent, and homogeneous. These properties, however, began to change in the very early stages of the aging−evaporation process. Figure 2 shows

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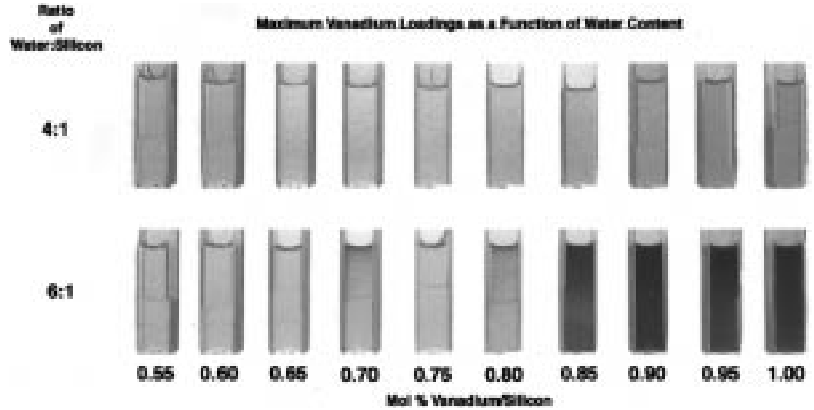

Figure 3. Gels of varying mol % vanadium−silicon, made with 4:1 and 6:1 water-to-silicon ratios and aged at 15% relative humidity, approximately one-quarter of the way through the aging-evaporation process.

samples containing 0.5% vanadium with water-to-silicon ratios of 3, 4, 6, 8, and 11 to 1 that were aged and dried under the two different humidity conditions. The samples in Figure 2 were approximately one-quarter of the way through the aging−evaporation process. Clearly, there was a rather dramatic change in the properties of the gels in going to high water and humidity. At the lower water levels, the gels were transparent, homogeneous, and almost colorless. As the water content increased, they became more intensely orange in color but retained their transparency. At a critical water level, which varied proportionally with humidity, the gels became dark green. The onset of this green color was accompanied by the onset of heterogeneity in that they became exceedingly opaque. The onset of heterogeneity occurred at lower water ratios for the higher humidity aging condition. These observations signal a strong relationship between the properties of the hybrid gels, in particular the homogeneity, and the water content. It also suggests that by controlling water content higher vanadium concentrations can be incorporated while still retaining homogeneity.

This suggestion was explored by preparing a series of sols of varying vanadium content at low and intermediate water concentrations. Figure 3 show a series of vanadium concentrations ranging from 0.55 to 1 mol % at 4 and 6 to 1 water-to-silicon ratios observed approximately one-quarter of the way through the aging-evaporation process. At this point in the process, formation of the green heterogeneous phase was observed at 0.85 mol % vanadium and above for the 6:1 water-to-silicon ratio samples, while materials made with 4:1 water-to-silicon ratio were homogeneous through the entire range of concentrations. These materials continued to change during the aging−evaporation process. By the end, vanadium concentrations as low as 0.5% had become heterogeneous when made with 6:1 water, while all of the samples made with 4:1 water-to-silicon ratio remained homogeneous. By lowering the water to a 3:1 water-to-silicon ratio, we were able to make homogeneous, transparent materials up to 1.5 mol % in vanadium.

At the conclusion of the aging−evaporation process the samples had decreased in size to about 10% of their original volume while approximately retaining the aspect ratio of the original mold. By this point the gels had ceased to change visually. Transparent homogeneous orange xerogels are realized for the conditions of low water and humidity, while at high water and humidity they were heterogeneous, green, and extremely opaque (Figure 4). The aged xerogels were then dried by heating gradually to 500 °C. Treatment at this temperature acts to remove adsorbed water and alcohol, to oxidize remaining organic matter (i.e. unreacted alkoxy groups), and otherwise to stabilize the xerogel.[25] After this thermal treatment, the homogeneous materials retained their transparency but became colorless, while the green materials turned orange but remained opaque and heterogeneous.

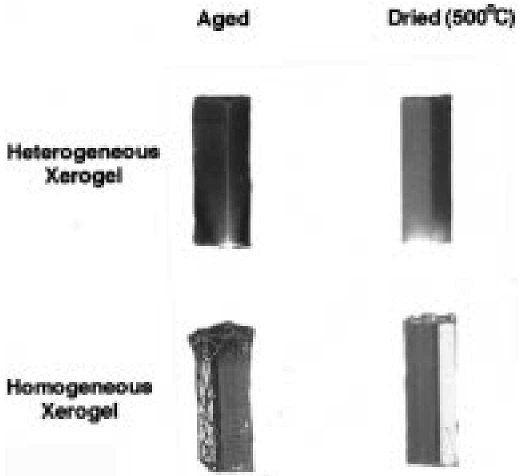

Figure 4. Heterogeneous and homogeneous xerogels after aging−evaporation and after drying at 500 °C.

Clearly, variations in the two parameters of water content and humidity have a profound effect on the distribution of vanadium in the final xerogel, which is reflected in the homogeneity. While we will not consider the coordination environment of the vanadium extensively here, a few comments are warranted concerning the nature of the green, heterogeneous material. Red polymeric vanadium pentoxide gels, which can be made by the direct hydrolysis of vanadium(V) alkoxides, have been observed to undergo slow conversion to a green material upon standing in air.[26] This green material has also been made in a controlled fashion by the partial reduction of the red vanadia gel with reductants such as Sb^{3+}.[27] This green, partially reduced material is

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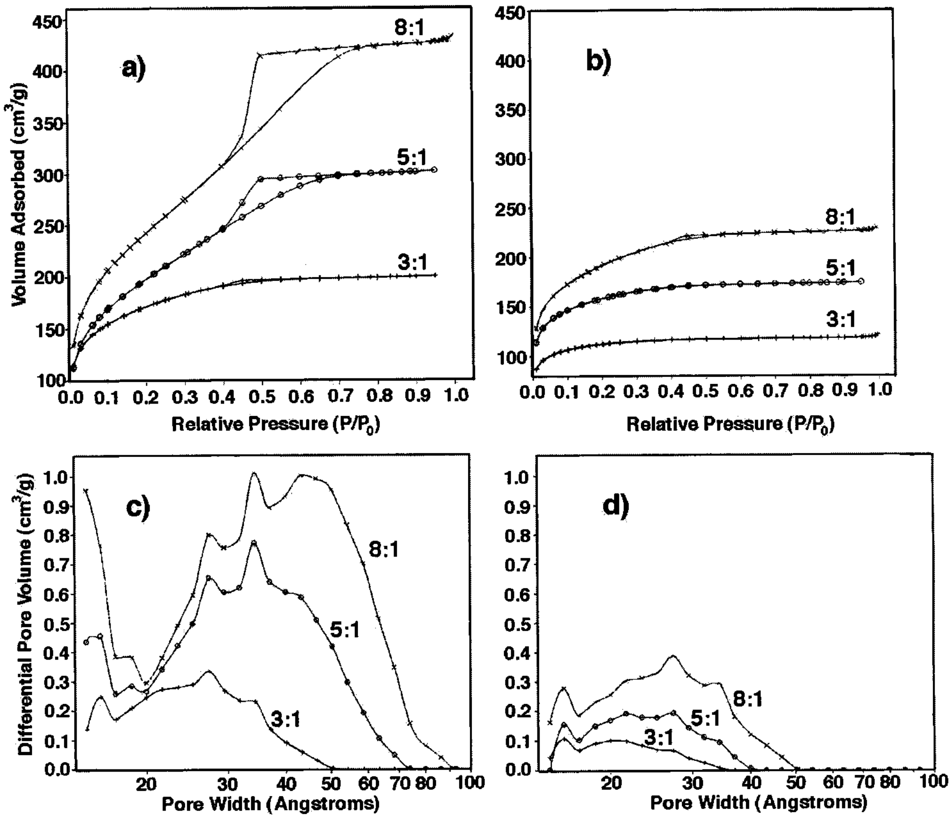

Figure 5. Nitrogen adsorption–desorption isotherms for (a) pure silica control and (b) 0.50 mol % vanadium–silicon dried xerogels and differential pore volume distributions for (c) pure silica control and (d) 0.50 mol % vanadium–silicon dried xerogels made with 3:1, 5:1, and 8:1 water-to-silicon ratios and aged at 15% relative humidity.

paramagnetic with an electron spin resonance (ESR) spectrum characteristic of axial V(IV) ($S = {}^{1}/_{2}$, $I = {}^{7}/_{2}$) with parallel and perpendicular **g** and **A** values close that of vanadyl(IV) pentaaquo.[28] These green materials also have an intense broad absorption at 1430 nm in the near-infrared which has been assigned to a V(IV) → V(V) intervalence band.[27] The spectroscopic characteristics of green vanadia–silica xerogels are virtually identical to those of the partially reduced pure vanadia gels. The electronic spectrum, collected by reflectance from a powdered sample, shows a strong broad band at 1438 nm. The material is ESR active, giving an anisotropic V(IV) spectrum with $g_{\|} = 1.935$, $g_{\perp} = 1.993$, $A_{\|} = 199$ G, and $A_{\perp} = 68$ G, which are very close to the values reported for the V(IV) sites in partially reduced vanadium pentoxide gels.[27,28] This suggests that, under conditions of high water and/or humidity, the vanadium tends to oligomerize with itself and form what are essentially vanadia gels in the pores of the silica. The vanadia gel undergoes partial reduction during the aging process, yielding the green material. Under the conditions studied in this investigation, heterogeneity was always accompanied by the formation of the green material. Materials that retained their orange color through the aging process remained homogeneous. This suggests that, under these conditions, optical heterogeneity is the result of the formation of a separate vanadia (or vanadia rich) phase in the xerogel. The formation of green material has also been reported in the sol–gel synthesis of vanadia–silica materials by sequential acid–base catalysis, though the optical heterogeneity of the final xerogel was not discussed.[6] It is entirely possible that, under other conditions, a green phase may form with the material retaining its optical transparency. Conversely, heterogeneity may occur without the onset of the green phase.

Morphological Properties of Vanadia–Silica Xerogels. While the water, humidity, and total vanadium content have a strong impact on the homogeneity, these parameters also influence the morphology of the bulk xerogel, in particular, its pore volume and surface area. Nitrogen adsorption–desorption isotherms for a series of pure silica and 0.5 mol % vanadium–silicon xerogels as a function of initial water content are shown in Figure 5. All samples had been aged at 15% humidity and dried at 500 °C. For pure silica, the isotherm at 3:1 water is of type I, indicating a largely microporous material, though evident are vestiges of a hysteresis loop, characteristic of capillary filling of mesopores. As the water content is increased, the volume of gas adsorbed increases, while the isotherms become progressively more characteristic of type IV, with the concomitant emergence of a hysteresis loop of type H2: all of which are indicative of a steady increase in the mesoporosity. The surface area, determined from the BET equation, increases with increasing water content as does the pore volume (Table 1). The increase in pore volume with increasing water for pure silica sol–gels is, of course, not a new observation. This trend was reported previously for both acid- and base-catalyzed xerogels.[20,29] The origin of the trend was attributed to an increase in the hydrolysis rate as water concentration

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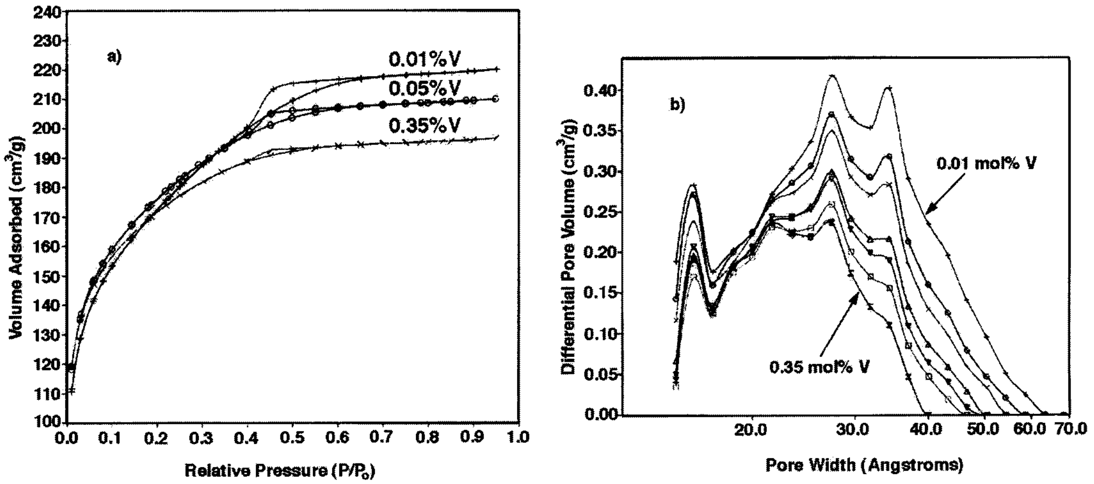

Figure 6. Nitrogen adsorption−desorption isotherms for (a) 0.01, 0.05, and 0.35 mol % vanadium−silicon xerogels. Differential pore volume distributions (b) for vanadium-to-silicon ratios ranging from 0.01 to 0.35 mol %. Between these extremes, the mole percents, in descending order, are 0.025, 0.05, 0.075, 0.10, and 0.15. Samples were made with an 8:1 water-to-silicon ratio, homogeneous, and aged at 15% relative humidity.

Table 1. Water Concentration Effects on the Porosity of Pure Silica and 0.5 mol % Vanadium−Silicon Xerogels[e]

H_2O:Si	surface area[a] (m^2/g)	pore volume[b] (cm^3/g)	micropore volume[c] (cm^3/g)	average pore size[d] (Å)
		Control Samples		
3:1	670(3)	0.28	0.12	17
4:1	712(7)	0.36	0.05	20
5:1	726(8)	0.39	0.05	22
6:1	739(11)	0.42	0.04	23
7:1	765(10)	0.44	0.04	23
8:1	876(11)	0.53	0.04	24
		0.50 mol % Vanadium Samples		
3:1	526(3)	0.20	0.15	15
4:1	563(2)	0.21	0.15	15
5:1	638(4)	0.25	0.15	16
6:1	678(3)	0.27	0.15	16
7:1	680(4)	0.27	0.14	16
8:1	651(5)	0.26	0.15	16

[a] Calculated from the BET equation; this equation is not strictly applicable to microporous materials. [b] Calculated from density functional theory. [c] Derived from *t*-plot analysis. [d] Average pore size = 4V/Å. [e] Samples were aged at 15% relative humiditity and dried to 500 °C.

Table 2. Effect of Vanadium Concentration on the Porosity of Vanadia−Silica Xerogels[e]

% V	surface area[a] (m^2/g)	pore volume[b] (cm^3/g)	micropore volume[c] (cm^3/g)	average pore size[d] (Å)
0.000	876(10)	0.53	0.04	24
0.010	617(5)	0.30	0.08	20
0.025	626(4)	0.29	0.10	19
0.050	637(4)	0.28	0.11	18
0.075	621(3)	0.26	0.13	17
0.10	626(3)	0.26	0.12	17
0.15	615(2)	0.25	0.13	16
0.25	577(4)	0.24	0.12	19
0.35	610(2)	0.24	0.14	16

[a] Calculated from the BET equation; this equation is not strictly applicable to microporous materials. [b] Calculated from density functional theory. [c] Derived from *t*-plot analysis. [d] Average pore size = 4V/Å. [e] Samples made with 8:1 water, aged at 15% relative humidity, and dried at 500 °C. All samples were homogeneous.

increases. The increased hydrolysis rate leads to an increased condensation rate and, hence, cross-linking of the polymeric chains. This cross-linking process causes the development of a particulate microstructure which is not as dense as materials with less cross-linking.

Analogous measurements of homogeneous xerogels made with the same water-to-silicon ratios, but containing 0.5 mol % vanadium, are dramatically different from the pure silica control samples. While an increase in adsorbed volume is observed with increasing water, all of the isotherms, regardless of water content, are unambiguously of type I with no evidence of hysteretic behavior until an 8:1 water-to-silicon ratio is reached, where vestiges of a hysteresis loop emerge. This suggests that, under identical conditions, the presence of vanadium results in a significantly more microporous material. Commensurate with this, the calculated surface areas and pore volumes are likewise greatly reduced in the materials containing vanadium, and the micropore volumes, estimated from *t*-plot analysis, are much larger (Table 1).

The large differences in pore structure between the pure silica and vanadia−silica samples can be seen graphically in the differential pore volume plots, which are calculated from the isotherms using density functional theory (Figure 5). As inferred from the type of isotherms and the size of the hysteresis loops, the pore size distribution in the pure silica materials become more mesoporous with increasing water content until, at an 8:1 water-to-silicon ratio, a significant amount of the total pore volume is in pores whose diameter is greater than 40 Å. For the materials containing vanadium, the total pore volume is significantly less, with a majority of that volume contained in pores of less than 40 Å in diameter.

Changes in the porosity as a function of vanadium concentration can be seen in Figure 6. Nitrogen adsorption−desorption isotherms and differential pore volume distributions as a function of vanadium concentration for samples made with an 8:1 water-to-silicon ratio, aged (15% humidity), and dried at 500 °C, show a systematic decrease in pore size with increasing amounts of vanadium. The effect is dramatic, with a large change in the isotherms and the differential pore

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(29) Brinker, C. J.; Scherer, G. W. *J. Non-Cryst. Solids* **1985**, *70*, 301.

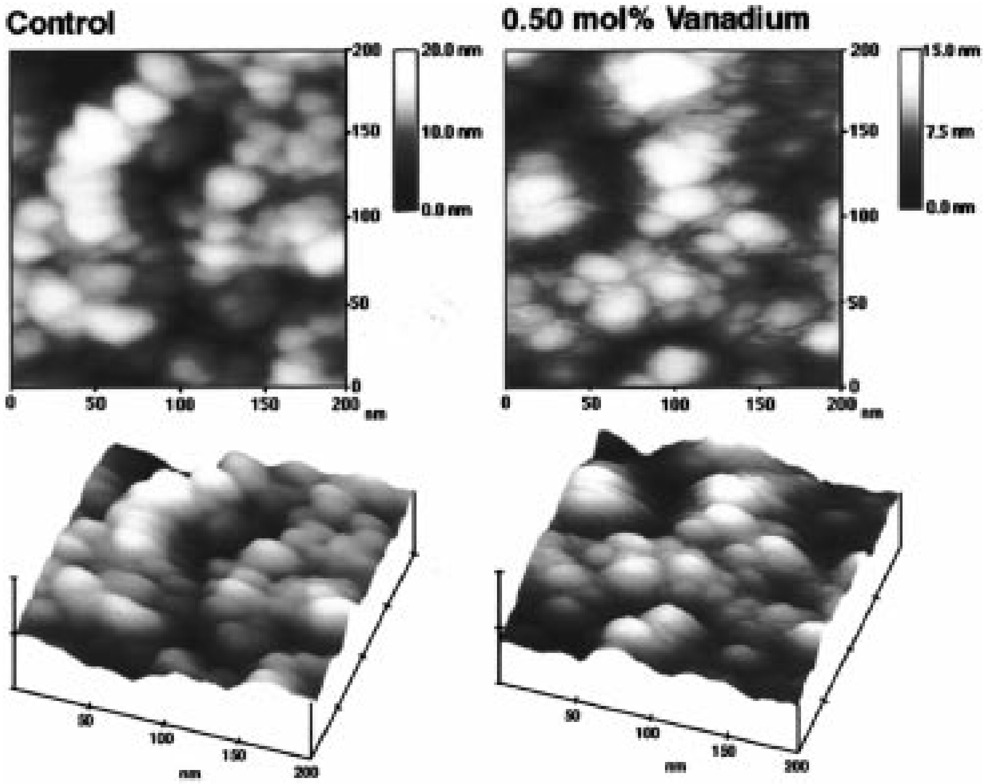

Figure 7. Atomic force micrographs, collected in tapping mode of the interior surface of freshly cleaved pure silica control and 0.5 mol % vanadium−silicon dried xerogels shown from top view (a) and oblique angle view (b). Samples shown were made with 3:1 water-to-silicon ratios and aged at 15% relative humidity.

size distribution observed even with the addition of very small amounts of vanadium. The isotherms vary as a function of vanadium content and go from type I with no hysteresis loop at high vanadium concentrations (0.35%) to a form approaching type IV with the appearance of a small type H2 hysteresis loop at low loadings (0.01%). However, even at low vanadium concentrations, the isotherms differ dramatically from the control sample, which is unambiguously of type IV with a large type H2 hysteresis loop. Notably, with increasing vanadium content there is little change in the BET surface area, although the surface area difference between the control and the 0.01 mol % sample is large. The total pore volume decreases with increasing vanadium content, as does the average pore diameter, while the micropore volume, estimated from the *t*-plot analysis, increases steadily (Table 2). The effect of vanadium concentration on the pore size distribution is both pronounced and nonlinear. There is a steady decrease in the number of pores greater than ~25 Å with increasing vanadium content, while the number of pores in the range below 25 Å remains relatively constant. Changes in the distribution of pore sizes saturated at about 0.35% vanadium, with little additional change observed at concentrations above that.

The pronounced effect of even small amounts of vanadium on the volume and size of the xerogel pores clearly has ramifications for the use of vanadia−silica xerogels in both sensor and catalytic applications in terms of mass transport to the vanadium sites. Differences in the microscopic structure of the pure silica and vanadia−silica xerogels were investigated by atomic force microscopy (AFM) in an attempt to understand the origin of the increased microporosity when vanadium is present. Figure 7 shows atomic force micrographs, collected in Tapping Mode, on the center of a freshly cleaved xerogel flat of a control and a 0.5% vanadium sample (3:1 water-to-silicon ratio, 15% humidity) over a 200 × 200 nm range. The morphology of the pure silica sample at this scale is typified by round, “pillowlike” or “globular” structures of relatively uniform size. Cross sectional analysis of the AFM scan allows the size of these structures to be estimated at around 20−25 nm. The pore structure represented by the voids between the packed pillowlike structures is on the order of 10 nm at the pore entrance. This diameter would decrease going further down between the pillows, out of the range of the AFM. This is, of course, mesoporous in dimension and is unlikely to account, to any significant extent, for the microporous volume determined from gas adsorption−desorption measurements. It is likely that the micropore volume is contained within the silica globules themselves, with the packing of these, in turn, giving rise to the mesopore volume. The morphology of pure silica xerogels formed from acid and base catalysis has been discussed extensively by Brinker and Scherer.[29] Formation of “globular” structures of similar dimensions, as measured by transmission electron microscopy, was observed in xerogels produced at high water or moderate pH (>2). The measured pH values for our uncatalyzed sols show them to be approximately neutral and, hence, fall into the range at which such morphology would be predicted.

The AFM image of xerogels containing 0.5% vanadium reveals the same basic morphology of packed “pillowlike” structures ~20−25 nm in diameter. Unlike the pure silica control samples, however, the regions between the structures in the 0.5% vanadia samples are not voids but are filled with material. These filled pores can be seen both in the flat and oblique angle (Figure 7) AFM views as high (light colored) irregular "lakelike" heterostructural regions formed around the pillow structures. The fact that the basic underlying silica morphology appears intact suggests that filling of the voids occurs later in the process than the formation of the primary silica globules and may represent chemistry that occurs well into the aging process. Consistent with this, Dutoit et al. observe an opposite trend in vanadia−silica low-temperature aerogels where a decrease in the microporous volume is seen with increasing vanadium concentrations. Since materials of this type are supercritically extracted with CO_2 directly after gelation and, therefore, do not go through the aging−evaporation process, this supports the contention that the onset of microporosity occurs during this stage of the process.[6,7]

The chemical makeup of these heterostructures is unknown. It might be suggested that the vanadium has phase-separated into bulk V_2O_5 regions in the xerogel. While these regions may very well be vanadium rich, it is unlikely that they are composed of the pure oxide. For one, there is no evidence of crystallinity from either microscopic or X-ray analysis. Furthermore, our previous spectroscopic studies on the same materials have supported discrete pseudotetrahedral oxovandium sites as the primary chromophore.[30] A possible explanation is that these regions are formed from oligomeric silica or silica−vanadia species that have remained fluid in the pores until late in the process. As discussed, the very long gelation time induced by the vanadium suggests that the rapid formation of extensive, high molecular weight silica species is inhibited. It is reasonable, therefore, to suggest that oligomeric species, prevented from completely polymerizing due to the inhibition of the vanadium, might build up and condense in the voids late in the process; possibly well after gelation. Regardless of the nature of these heterostructures, their filling of the voids in the silica matrix is undoubtedly the source of the reduction in pore volume and size when vanadium is present. Whether these structures exist under other typical sol−gel conditions (e.g. acid or base catalysis) and the degree to which they affect properties such as catalytic activity remains to be explored.

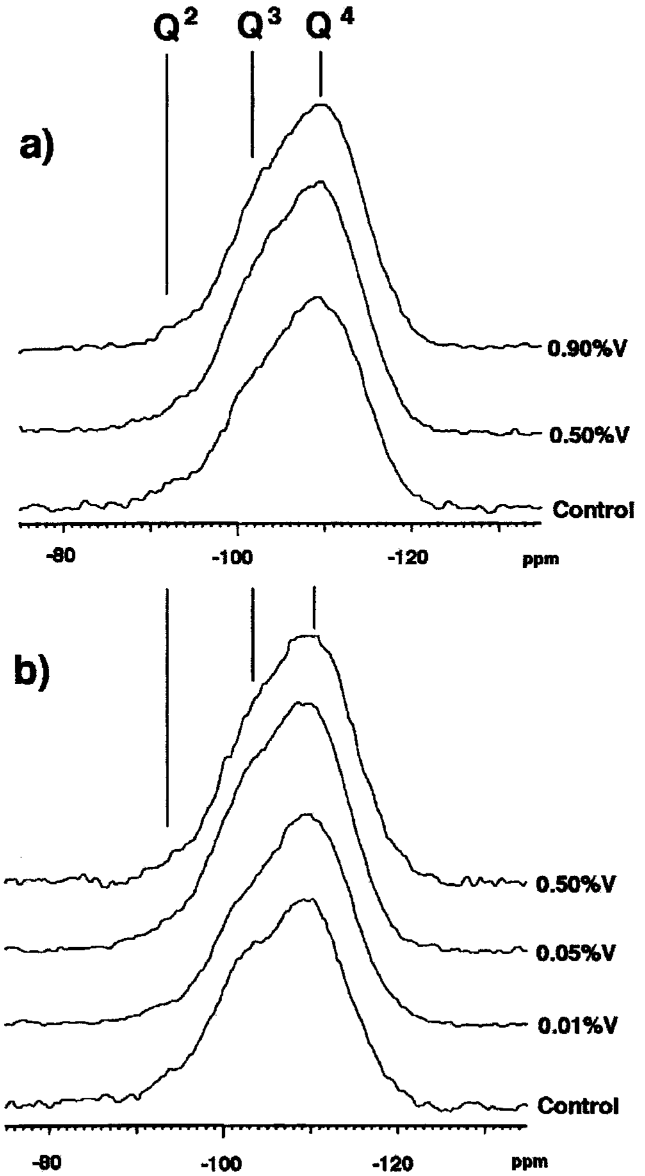

Figure 8. Solid-state ^{29}Si NMR spectra of pure silica and vanadia−silica dried xerogels made with (a) 4:1 and (b) 8:1 water-to-silicon ratios. The samples were aged at 15% relative humidity.

The effect of filling these voids is evident in the solid-state ^{29}Si NMR spectra of the processed xerogels. Figure 8 shows spectra for pure silica control samples and vanadia−silica samples of varying concentrations made with 8:1 and 4:1 water-to-silicon ratios. The pure silica control sample shows large peaks at −110 and −101 ppm and a small peak at −93 ppm (relative to tetramethylsilane). Using the conventional Q^n notation, where n indicates the number of bridging oxygens (OSi) around the silicon, these resonances correspond to Q^4, Q^3, and Q^2, respectively.[31] Only Q^4 would be expected in a fully dense glass; therefore, the presence of Q^3 and Q^2 resonances is indicative of incomplete cross-linking and, hence, less dense materials. In moving from 4:1 to 8:1 water, the pure silica control showed an increase in the relative amounts of Q^3 and Q^2, which is consistent with the increased mesoporosity observed at higher water. Addition of vanadium, even at concentrations as low as 0.01%, resulted in a marked decrease in Q^3 and Q^2 relative to Q^4. As the amount of vanadium increases, regardless of the water ratio, the Q^3 resonance ultimately recedes into a barely detectable shoulder on the dominant Q^4 band. This suggests a high degree of cross-linking, with the majority of silicon atoms bonded to four other OSi groups. This is consistent with the increasing microporosity determined from the gas adsorption−desorption measurements. It can be understood in terms of mesopore filling by oligomeric silica (or vanadia−silica) species which condense with an unreacted SiOH or SiOR group on the surface of the globular heterostructures, cross-linking between them to fill the pores. The net result of this is a conversion of uncondensed silica (Q^2 and Q^3) into more fully condensed (Q^4) material.

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(30) Tran, K.; Hanning-Lee, M. A.; Biswas, A.; Stiegman, A. E., Scott, G. W. J. *Am. Chem. Soc.* **1995**, *117*, 2618.

(31) Reference 18, p 101.

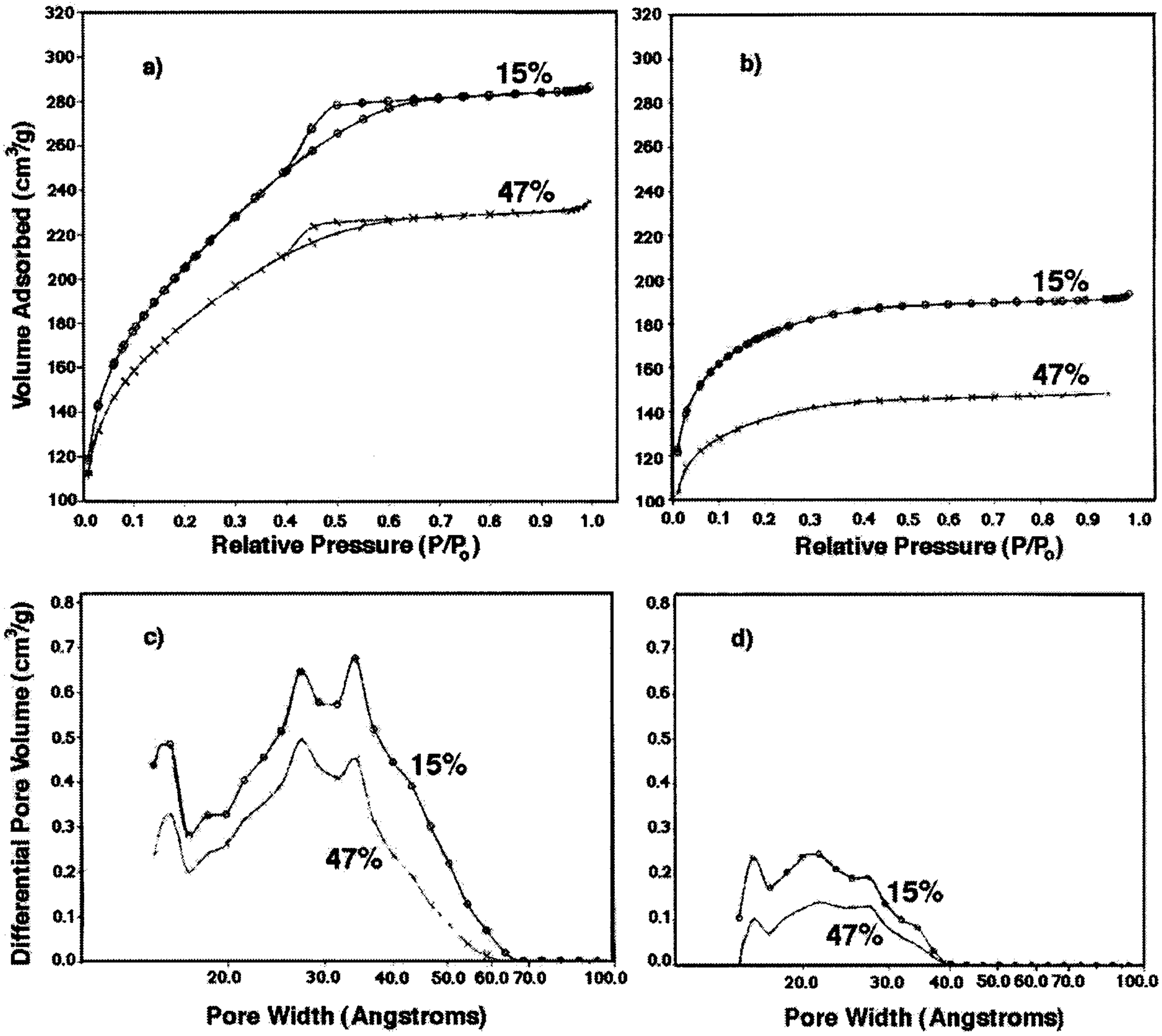

Figure 9. Nitrogen adsorption–desorption isotherms for (a) pure silica control and (b) 0.5 mol % vanadium–silicon xerogels and differential pore volume distributions for (c) pure silica control and (d) 0.5 mol % vanadium–silicon xerogels aged at 15% and 47% relative humidity. Samples were made with a 5:1 water-to-silicon ratio.

Table 3. Humidity Effects on the Porosity of Silica and 0.5 mol % Vanadium–Silicon Xerogels[e]

	surface area (m^2/g)	pore volume (cm^3/g)	micropore volume (cm^3/g)	average pore size (Å)
	Control Samples			
15%	726(8)	0.39	0.05	22
47%	640(6)	0.32	0.07	20
	0.50 mol % Vanadium Samples			
15%	638(3)	0.25	0.15	16
47%	507(2)	0.19	0.13	15

[a] Calculated from the BET equation; this equation is not strictly applicable to microporous materials. [b] Calculated from density functional theory. [c] Derived from *t*-plot analysis. [d] Average pore size = 4V/Å. [e] Samples made with 5:1 water and dried at 500 °C. All samples are homogeneous.

Humidity Effects on Morphology. The effect of the humidity under which the aging–evaporation process is carried out has an effect on the morphology of both the pure silica control samples and the vanadia–silica materials. The influence of humidity at this stage of the sol–gel process, while not as dramatic as the effect of added water, is nonetheless observable. In general, the silica control samples showed a decrease in pore volume and surface area with increasing humidity. This trend was evident in all the samples, regardless of water content, but became more pronounced at higher water concentration. Figure 9 shows isotherms for representative samples made with a 5:1 water-to-silicon ratio, aged at 15% and 47% relative humidity. The isotherms for these samples show a transition from a type IV isotherm with a H2 hysteresis loop at low humidity to a form approaching type I but still with a small hysteresis loop at high humidity. These changes in the isotherms are reflected in the values calculated from them (Table 3). The BET surface area and the pore volume decrease as the humidity increases. These trends can also be seen graphically in the pore size distribution, where a decrease in the number of pores above ~30 Å is observed with increasing humidity.

The materials containing vanadium are inherently more microporous than the pure silica controls prepared under identical conditions. As such, the effect of humidity on the porosity is not nearly as pronounced and is less affected by the initial water content of the sample. Both of the isotherms are of type I, with no indication of hysteretic behavior. There are only small changes in the parameters calculated from the isotherms (Table 3) though the trend is the same with a

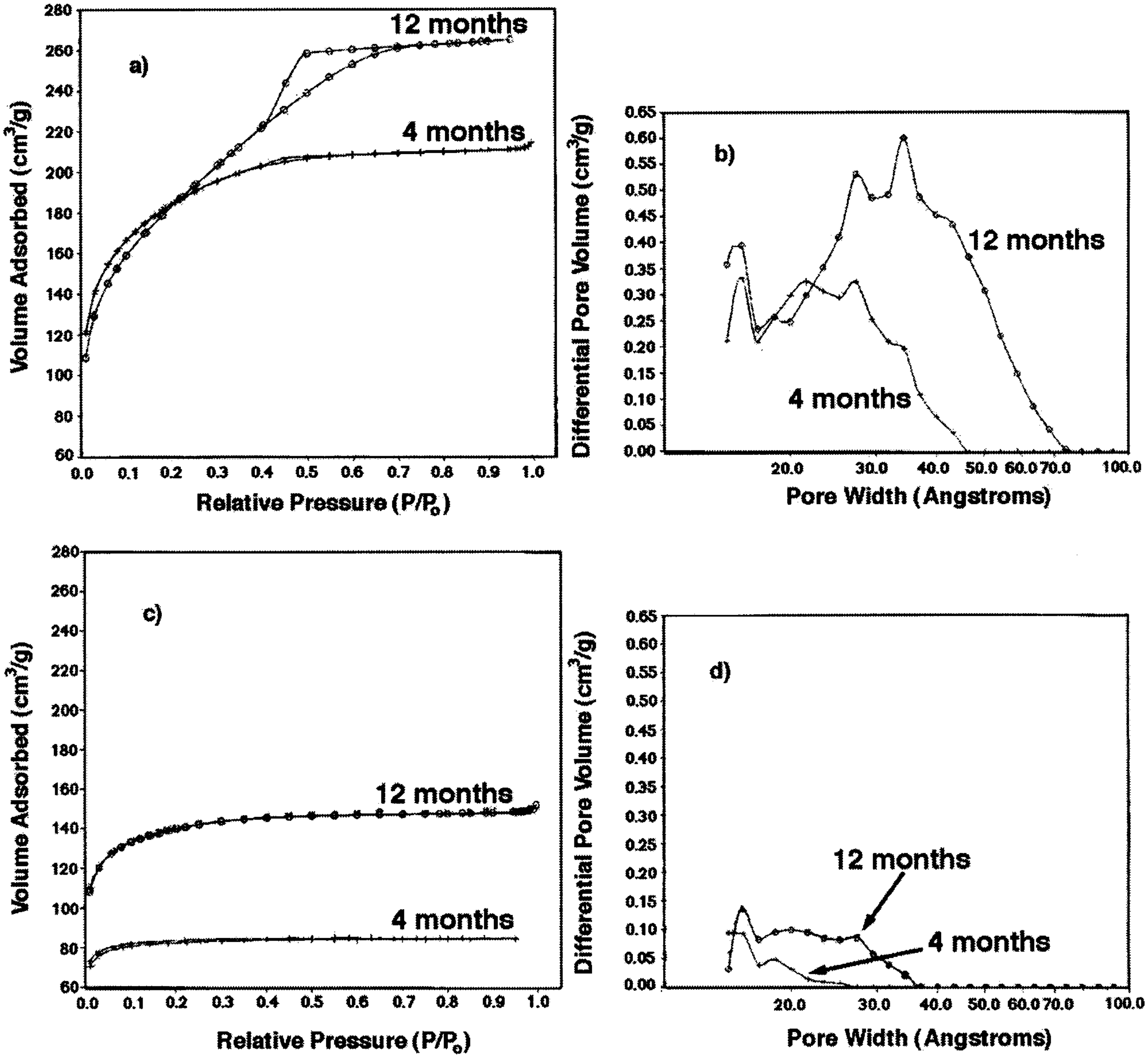

Figure 10. Nitrogen adsorption−desorption isotherms for (a) pure silica control and (b) 0.5 mol % vanadium−silicon xerogels and differential pore volume distributions for (c) pure silica control and (d) 0.5 mol % vanadium−silicon xerogels aged for 4 and 12 months. Samples were made with a 3:1 water-to-silicon ratio and aged at 15% relative humidity.

decrease in BET surface area and pore volume and a small increase in micropore volume with increasing humidity. In short, while humidity can have a strong impact on the homogeneity of the vanadia−silica xerogels, it exerts only a modest effect on the morphology. It seems likely that the origin of the trend in both pure and loaded samples arises from the availability of water to continue to drive condensation reactions between remaining SiOH and SiOR groups, which acts to further condense the gel. At low humidity, the steady-state concentration of water is low, impeding further condensation and yielding more mesoporous materials. The converse is true at higher humidity.

One aspect of humidity-controlled aging and drying that must be taken into account is the time the gel takes to complete the process. The total aging time differs considerably depending on the humidity under which the process is carried out. For example, aging times for samples aged at 15% humidity were approximately 4 months, while those at 47% relative humidity required approximately 10 months (the times varied somewhat with the water-to-silicon ratio of the sample). This difference in aging times raises the question of to what extent is the observed humidity dependence due solely to humidity. To investigate this, a control sample and a 0.5% vanadium−silicon sample, made with varying water-to-silicon ratios, were prepared. After gelation, the cap was removed from one sample following our usual protocol, while the other sample was punctured with a 16-gauge disposable syringe needle. They were then aged in a 15% relative humidity chamber. The constriction imposed by the syringe needle greatly lengthened the aging time at that fixed humidity. The samples with the cap removed had completed the process in around 3 months while the punctured sample was completed in 12 months. Figure 10 shows nitrogen adsorption−desorption isotherms for a representative sample (15% humidity; 3:1 water-to-silicon ratio) of the pure silica control and 0.5% vanadium−silicon xerogels at the two different aging times. For the control samples the isotherms are of type I with no hysteresis loop at short aging times and are of type IV with a hysteresis loop at long aging times, indicative of increasing mesoporosity. Consistent with this, the differential pore size distribution shows an increase in the number of pores above ∼35 Å at the longer aging time.

The vanadia−silica materials, which are initially much more microporous, show similar, though far less dramatic, differences as a function of aging time. Both of the isotherms are of type I with the shorter aged sample adsorbing less total volume. The pore size distribution shows an increase in pores above ∼25 Å with increased aging time. Notably, the observed trend in aging time runs counter to the trend observed for the two different humidities where high humidity conditions, which have long aging times, have smaller pore volumes and are more microporous. This result suggests that the decrease in porosity at higher humidity is indeed due to the humidity and not simply to the longer aging times that necessarily accompany it. More significantly, however, it suggests that the final morphology of the xerogel is dictated by a complex combination of all of the factors described: water content, humidity, vanadium concentration, and aging time.

A number of general conclusions can be made from the data presented in this study. Clearly, the conditions under which the sol−gel process is carried out, specifically water content and aging conditions, strongly affect the distribution of the vanadia in the xerogel matrix, as is evidenced by the macroscopic homogeneity that occurs under certain conditions. Conversely, the presence of vanadium in the sol−gel system exerts a profound influence on the gelation time and on the morphological properties of the processed xerogel. Taken together, these effects can be varied in concert to produce either homo- or heterogeneous materials with varying amounts of vanadium and porosities ranging from very microporous to slightly mesoporous. However, there is an obvious tradeoff between porosity and vanadium content. The higher the vanadium loading, the more microporous the material becomes. While high water concentrations can be used to increase the mesoporosity, the amount of vanadium that can be incorporated under those condition is limited due to the formation of the green, heterogeneous phase.

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