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Vanadia/Silica Xerogels and Nanocomposites

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The application of the sol–gel process to the synthesis of dense oxide glasses and ceramics has been the subject of escalating interest because of the low temperatures and compositional flexibility inherent in this purely chemical approach. More recently it has been realized that undensified silica "xerogel" materials possess unique properties precisely because of their porous nature. We report here the synthesis of a new transparent metal containing silica gel by the co-condensation of low concentrations of oxovanadium triisopropoxide with tetraethylorthosilicate (TEOS) via the sol–gel process.[1] This co-condensation results in the covalent bonding of discrete, isolated pseudotetrahedrally coordinated oxovanadium(V) functional groups into the silica framework. The presence of these groups and the particular reactivity associated with them impart a number of unique properties to the bulk material including color changes that result from the coordination of small molecules, thermal and photochemical oxidation/reduction processes, and the photoinitiated polymerization of organic monomers inside the silica gel matrix. While metal/silica xerogels have been investigated in the past, to the best of our knowledge, no previous single example has shown this diverse combination of properties.[2]

Low concentrations of oxovanadium triisopropoxide were used in the hydrolysis/condensation reaction to ensure that homogeneous bulk materials were produced and that discrete monomeric vanadium oxide groups were distributed throughout:

$$m\mathrm{Si(OEt)_4} + n(i\text{-}\mathrm{PrO})_3\mathrm{VO} + {}^7\!/_2(m+n)\mathrm{H_2O} \rightarrow [\mathrm{Si}_m\mathrm{V}_n\mathrm{O}_{2m+2.5n}] + 4m\mathrm{EtOH} + 3n(i\text{-}\mathrm{PrOH}) \qquad n/m \le 0.5\%$$

The reaction was carried out in 1-cm polystyrene cuvettes which were sealed and allowed to gel.[3] After gelation, the seals were punctured and the materials were allowed to age for approximately 6 months, after which remained transparent xerogels flats approximately 0.4 × 0.4 × 1.25 cm in dimension and ranging from colorless to dark orange (Figure 1a) with increasing vanadium con-

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(1) Brinker, C. J.; G. Scherer, G. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*; Academic Press: Boston, 1990.

(2) Many of the materials made previously by the co-condensation of transition metals and silicon alkoxides have utilized relatively high metal concentrations and are often sintered into dense glasses—characteristics that would preclude observation of many of the properties we describe here. TiO_2/silica sol–gels have been described extensively because of their importance as low thermal expansion glasses ((a) ref 3; p 226). Similarly, a good deal of work has also been reported on ZrO_2 silicas ((b) Kamiya, K.; Sakke, S.; S.; Tatemichi, Y. *J. Mater. Sci.* **1980**, *15*, 1756. (c) Salvado, I. M. M.; Serna, C. J.; Navarro, J. M. F. *J. Non-Cryst. Solids* **1988**, *100*, 330). Recently the properties of several SiO_2/V_2O_5 materials have also been reported, including the bulk properties of densified glasses ((d) Ghosh, A.; Chakravorty, D. *Appl. Phys. Lett.* **1991**, *59*, 855. (e) Tohge, N.; Moore, G. S.; Mackenzie, J. D. *J. Non-Cryst. Solids* **1984**, *63*, 95). Baiker *et al.* have described the selective catalytic reduction of nitric oxide with stabilized SiO_2/V_2O_5 xerogels that, at their lowest vanadia concentration, are similar to the materials described here. Interestingly, it was the lower V^{5+} concentrations (1–10%) that showed the highest specific activities ((f) Baiker, A.; Dollenmeier, P.; Glinski, M.; Reller, A.; Sharma, V. K. *J. Catal.* **1988**, *111*, 273).

(3) V/Si ratios of 0.005–0.5% were made by adding the desired quantity of a 0.042 M solution of oxovanadium triisopropoxide in isopropyl alcohol to 6 mL (0.027 mol) of TEOS. Isopropyl alcohol was then added to bring the total volume to 12 mL, at which point 8 mL of a $^1/_3$ isoproyl alcohol/water mixture were added dropwise while sonicating. 4-mL aliquots were placed into 1-cm polystyrene cuvettes, sealed, and allowed to gel. No catalyst was used, and gelation occurred in about 2 weeks at room temperature.

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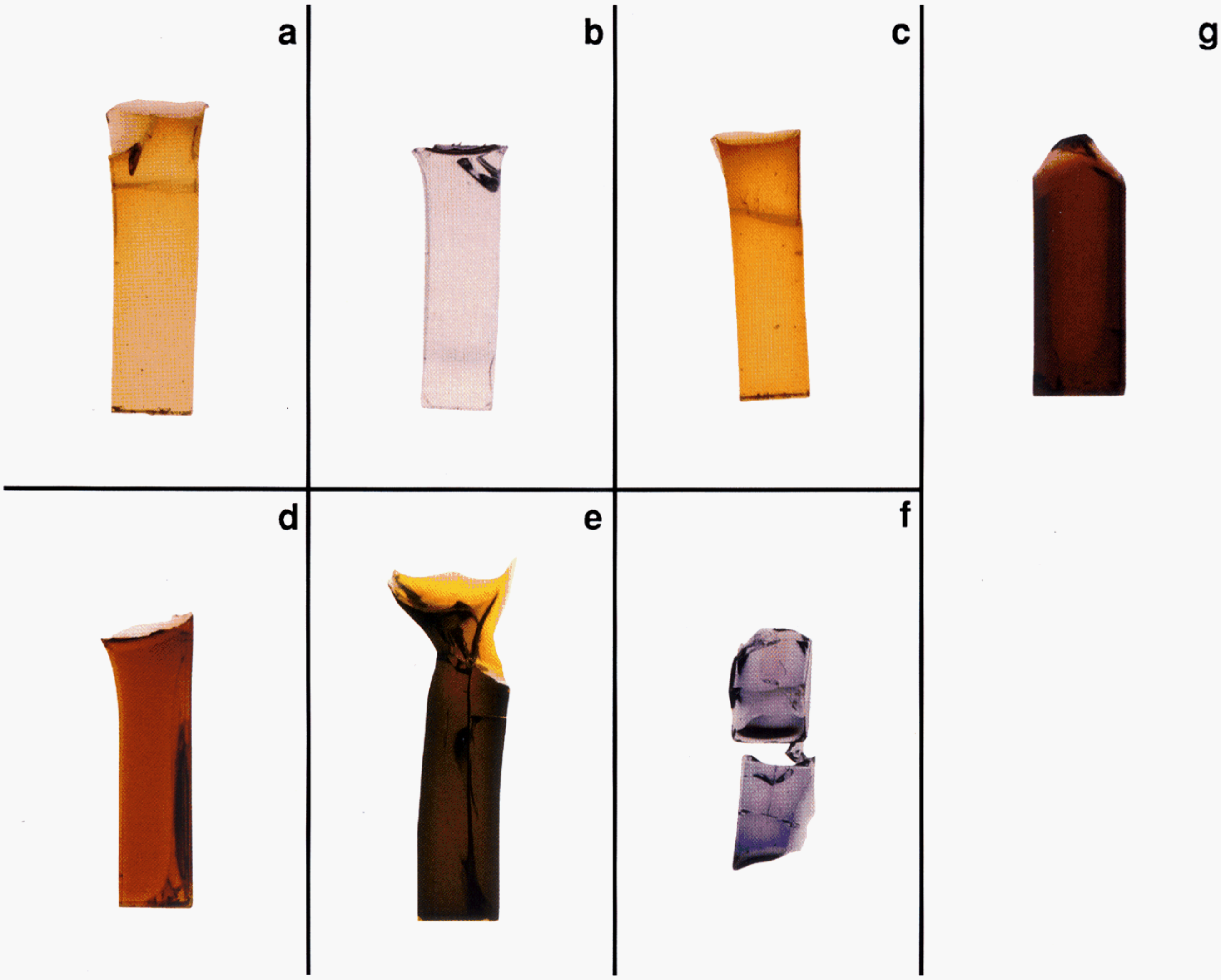

Figure 1. Observed color of 0.5 mol % vanadia–silica xerogel: (a) aged, (b) dried, and stabilized, (c) hydrated, (d) after sorption of hydrogen sulfide, (e) after sorption of formic acid (f) after hydrogenation (reduction), and (g) after photopolymerization of acetylene.

centration. The orange color of the xerogels remained after drying (125 °C, 1 week); however, upon stabilization[4] at 500 °C for 3 days all of the materials, regardless of vanadium concentration, became colorless (Figure 1b).

The specific coordination environment of the vanadium in the silica matrix was probed directly by solid-state ^{51}V NMR spectroscopy.[5] The NMR spectra of a stabilized xerogel containing 0.5 mol % V are shown in Figure 2. The static spectrum of the dehydrated material reveals an axially symmetric chemical shift tensor with $\delta_{\parallel}$ and $\delta_{\perp}$ values of -1250 ± 50 and -500 ± 20 ppm vs $VOCl_3$, respectively. Previous studies of discrete vanadium compounds with known local environments have shown that the anisotropic chemical shift properties of the ^{51}V nucleus are highly diagnostic of the coordination geometry.[6] In particular, the line shape observed for the dehydrated sample (Figure 2b) is unique to a pseudotetrahedral $O{=}VO_{3/2}$ coordination environment and has been previously observed for vanadium oxide monolayers on a dehydrated SiO_2 surface.[7] Furthermore, an intense transition in the FT-IR spectrum at 935 cm^{-1} is also observed. This transition, which is absent in pure silica and whose intensity depends on the vanadium concentration, is characteristic of terminal vanadium–oxygen bonds.[8] Taken together, these results suggest that the structure of the vanadium in the silica framework is one of local pseudotetrahedral geometry possessing a short terminal (V=O) bond and three long vanadium oxygen bonds which are connected to the silica (V–O–Si, Figure 2b, inset).

Exposure of the stabilized xerogels to humidity results in a rapid weight gain from the uptake of water and a concomitant color change from colorless to orange (Figure 1b,c). The evolution of the UV–vis spectrum as a function of water absorption is shown in Figure 3. The spectrum of the dehydrated materials shows an intense transition appearing as a shoulder at 235 nm ($\epsilon = 8 \times 10^3$) which diminishes in intensity as water is absorbed, while a low-

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[4] Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33.

[5] Solid-state ^{51}V NMR spectra were observed at 79.0 MHz using a General Electric GN-300 spectrometer equipped with an Explorer fast digitizer and a probe from Doty Scientific. A solid echo (θ–τ–2θ) sequence was used, where θ corresponds to a selective 90° pulse of 1.5-μs length. The τ delay was set to 50 μs and typically 200 000 transients were averaged with a recycle delay of 500 ms. The time-domain data were left-shifted to the top of the echo, zero-filled, and multiplied with an exponential filter function corresponding to a line broadening of 2000 Hz prior to Fourier transformation. Chemical shifts were reported using $VOCl_3$ as an external reference.

[6] Eckert, H.; Wachs, I. *J. Phys. Chem.* **1989**, *93*, 6796.

[7] Das, N.; Eckert, H.; Hu, H.; Wachs, I.; Walzer, J.; Feher, F. *J. Phys. Chem.* **1993**, *97*, 8240.

[8] Hardcastle, F. D.; Wachs, I. *J. Phys. Chem.* **1991**, *95*, 5031.

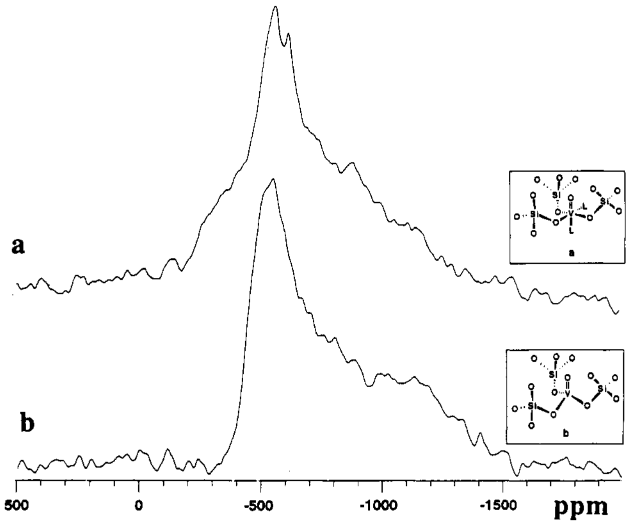

Figure 2. 79.0-MHz solid-state ^{51}V NMR spectra and deduced geometry (inset) of (a) hydrated and (b) desiccated 0.5 mol % vanadia–silica composite.

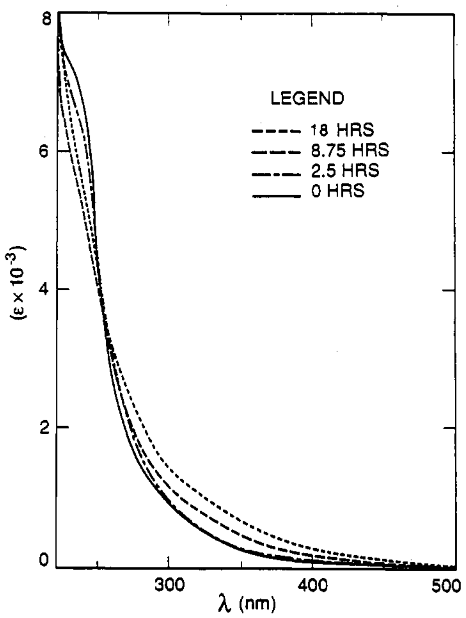

Figure 3. Absorption changes observed for a dried 0.005 mol % vanadia–silica optical flat when exposed to an environment of 100% relative humidity.

energy shoulder at ~340 nm emerges. These spectral changes are due to direct coordination of the water molecules to the vanadium metal center which converts the pseudotetrahedral environment to one of higher coordination number. The tendency of pseudotetrahedral V^V compounds to increase their coordination sphere by either adding ligands or through oligomerization is well documented as are the color changes associated with it.[9,10]

Coordination of water molecules to the vanadium center can be observed by the solid-state ^{51}V NMR spectrum of the fully hydrated material. In addition to the dominant feature near −520 ppm, the hydrated material also shows a distinct shoulder at −350 ppm (Figure 2a), which is highly diagnostic of octahedral V^V (Figure 2a, inset).[6] Extensive model compound studies have shown that all octahedrally coordinated vanadium–oxygen compounds possess their most intense solid-state NMR line-shape components in this frequency region. As discussed previously, this feature reflects the perpendicular component of a nearly axially symmetric chemical shift tensor. The presence of a significant amount of residual pseudotetrahedral V^V, even after extensive hydration, suggests that not all of the oxovanadium(V) groups may be easily accessible to entering ligands. The association of water is completely reversible with the coordinated water being driven off at ≥175 °C, returning the material to its colorless form. Multiple cycles of this process do not appear to degrade the material. In essence, the vanadium centers undergo the first step of hydrolysis, binding of water, but as it is stabilized by the silica matrix, no further chemistry can take place.[11]

Other small molecules also coordinate to the vanadium center, often imparting a characteristic color to the material. For example, Figure 1d,e show the deep amber and dark green materials that are formed by the association of hydrogen sulfide and formic acid, respectively. In addition, ammonia is observed to turn the material very pale yellow, while formaldehyde-coordinated material is bright yellow. The material also exhibits a distinct coordinating preference along with these chemical sensing properties. The sorption of formaldehyde appears to be favored over that of water, which in turn is clearly favored over that of ammonia.

In addition to coordination chemistry, oxidation/reduction transformations can also be carried out at the vanadium centers. The stabilized vanadia/silica xerogels turns deep sapphire blue when exposed to hydrogen gas at 490 °C (Figure 1f) due to the reduction of V^V to V^{IV}.[12] The presence of V^{IV} was confirmed by electron spin resonance (ESR) spectroscopy due to its characteristic eight-line spectrum resulting from hyperfine coupling to the ^{51}V nucleus. Anisotropic g values ($g_\parallel = 1.9203$, $g_\perp = 1.9822$) and hyperfine splittings ($A_\parallel = 555.7$ MHz, $A_\perp = 210.6$ MHz) determined from the spectrum are diagnostic of V^{IV} in, at highest, a cylindrically symmetric crystal field.[13] In addition, FT-IR spectra show an attenuation, albeit not a complete elimination, of the 935-cm^{-1} V=O stretch after hydrogenation. This suggests that, as with the coordination processes discussed previously, not all vanadium centers are reactive. The reduction can also be carried out photochemically with irradiation ($\lambda > 305$ nm) at room temperature under an atmosphere of hydrogen yielding the same blue color and characteristic ESR spectrum as the thermally reduced material. Hydrogen atoms can also be identified in the ESR spectrum by their characteristic two-line spectrum at $g = 2.0023$ separated by 505.9 G when the irradiation is carried out at 77 K.[14] We have determined that this photochemical reaction also extends to organic hydrocarbons—in particular, methane

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[9] (a) Crans, D. C.; Chen, H.; Felty, R. *J. Am. Chem. Soc.* **1992**, *114*, 4543. (b) Crans, D. C.; Chen, H.; Felty, R.; Eckert, H.; Das, N. *Inorg. Chem.*, submitted for publication. (c) Nabavi, M.; Sanchez, C. *Compt. Rend.* **1990**, *310*, 117. (d) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978.

[10] (a) Cartan, F.; Caughlan, C. *J. Phys. Chem.* **1960**, *64*, 1756. (b) Lachowicz, V.; Höbold, W.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1975**, *418*, 65. (c) Madic, C.; Begun, G.; Hahn, R.; Launay, J.; Thiessen, W. *Inorg. Chem.* **1984**, *23*, 469. (d) Lemerle, J.; Nejem, L.; Lefebvre, J. *J. Inorg. Nucl. Chem.* **1980**, *42*, 17.

[11] Livage, J. *Chem. Mater.* **1991**, *3*, 578.

[12] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980; p 715.

[13] (a) Tougne, P.; Legrand, A. P.; Sanchez, C.; Livage, J. *Phys. Chem. Solids* **1981**, *42*, 101. (b) Chasteen, N. D. In *Biological Magnetic Resonance*; Plenum Press: New York; 1981; Vol. 3, Chapter 2 pp 53–110.

[14] Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance, Elementary Theory and Practice*; McGraw-Hill: New York, 1972; p 442.

gas. Photolysis ($\lambda > 305$ nm) of a 0.5 mol % vanadia/silica xerogel under an atmosphere of methane gives a blue material with an identical ESR spectrum to that obtained from hydrogen reduction. When the reaction is carried out at 77 K, a spectrum characteristic of methyl radicals ($g = 2.0031$; $A = 23.0$ G) is detected.[15] The methyl radicals persist at 77 K in the silica matrix but disappear upon warming to room temperature.[16] Gas chromatographic analysis of the products verified the presence of ethane, the expected product of methyl radical recombination, and trace amounts of propane resulting from subsequent atom-abstraction recombination processes. While thermal and photochemical methane activation has been reported previously for metal oxide materials including supported V_2O_5,[17,18] this is the first report in a sol–gel material. Furthermore, these results suggest that the excited state of the discrete oxovanadium centers in the silica matrix are potent oxidants.[19]

In all cases, the reduced vanadium is rapidly reoxidized upon exposure to air, as is evidenced by the immediate fading of the characteristic blue color along with the rapid disappearance of the ESR signal. In fact, irradiation of the material under a 1/1 CH_4/O_2 mixture (1 atm) in the ESR cavity showed formation of methyl radicals, but no V(IV) species were observed. The redox reversibility suggests that pseudotetrahedral V=O sites serve as catalytic centers, a fact confirmed by recent studies on vanadium silicalite zeolites.[20,21]

Oxovanadium(V) molecules have been shown to photoinitiate vinyl polymerization.[22] This property is retained in the xerogels where the V=O sites photoinitiate the polymerization of gaseous monomers inside the pore structure of the stabilized xerogel.[23] In this way we have photopolymerized acetylene to form a new example of a conjugated polymer/silica nanocomposite. Specifically, stabilized 0.5 mol % vanadia/silica xerogels were evacuated (10^{-5} Torr) and back-filled to 1 atm with acetylene gas. Immediately upon exposure to light ($\lambda > 300$ nm) the material turned to the deep red color (Figure 1g) characteristic of polyacetylene. The presence of the *trans* isomer is confirmed by the Raman spectrum which shows two characteristic peaks at 1513 cm^{-1} (C=C) and 1126 cm^{-1} (C—C).[24] While other types of conjugated polymers have been generated inside of sol–gel glasses[26] and acetylene itself has been polymerized inside the channels of zeolites,[27] to the best of our knowledge this is the first example of its integration into a optically transparent silica matrix.

The vanadium/silica xerogels described in this report possesses a number of unique properties due to the sequestering of discrete oxovanadium centers in the silica xerogel. This imparts the reactivity of that functional group to the otherwise inert matrix which in turn serves to stabilizes the oxovanadium center against secondary reactions. This synergism produces a new material with diverse properties potentially suitable for a variety of applications.

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Supplementary Material Available: Raman spectrum of vanadium–silica/*trans*-polyacetylene nanocomposite (1 page). Ordering information is given on any current masthead page.

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(23) This material is an interesting addition to the broad category of polymer ceramic/glass nanocomposites which have been the subject of much recent attention (see for example: Kanatzidis, M. G.; Bissessur, R.; DeGroot, D. C.; Schindler, J. L.; Kannewurf, C. R. *Chem. Mater.* **1993**, *5*, 595 and references therein).

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