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Synthesis and Electronic Properties of Low-Dimensional Bis(benzene) Vanadium Reduced Mesoporous Niobium Oxide Composites

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The first bis(benzene) vanadium mesoporous niobium oxide composite was synthesized and characterized. The XRD pattern of this material shows a peak (100) centered at 45 Å, identical to that of starting material. The nitrogen adsorption and desorption analyses of this material exhibit a slight decrease of BET surface area from 580 $m^2 g^{-1}$ to 467 $m^2 g^{-1}$ and a concomitant decrease in pore size and volume from 28 Å and 0.500 $cm^3 g^{-1}$ to 25 Å and 0.363 $cm^3 g^{-1}$, respectively. The powder EPR spectrum shows eight lines which can be assigned to ^{51}V from bis(benzene) vanadium as well as other resonances that can be assigned to the corresponding cation. The presence of two or more organometallic vanadium species was further confirmed by UV, ^1H-MAS NMR, and XPS methods. Broadened and shifted Nb $^3/_2$,$^5/_2$ peaks were also observed, providing further evidence that the mesoporous transition metal oxide framework was reduced by the organometallic. SQUID magnetometer measurements on this material show paramagnetic behavior with a small contribution of spin glass behavior. The conductivity of this material was 10^{-4} ohm^{-1} cm^{-1}, significantly greater than that measured for the analogous bis(benzene) chromium composite previously studied. Since alkali-metal reduced mesoporous niobium oxide materials are insulating, this conductivity was attributed to the low-dimensional bis-arene vanadium phase in the pores and rationalized according to the balance between the Hubbard potential and the bandwidth estimated for the relevant organometallic species. A bis-1,3,5-tri-*tert*-butylbenzene yttrium composite was also synthesized; however, complete loss of ligand upon reduction of the mesostructure was observed, indicating that this dopant behaves more like an alkali naphthalene reagent in its reactions with mesoporous niobium oxide than other bis(arene) complexes investigated by our group.

Introduction

There is much current research interest in the fabrication of nanostructured composites because materials with limited dimensionality and periodic features on the nanometer level often possess properties that are not normally observed in bulk samples of the same material.[1,2] While zeolites serve as effective hosts for the confinement of nanometer-sized grains for catalytic and physical studies,[3,4] their maximum pore size limit of 15−18 Å makes it difficult to use them as hosts for materials with unit cells that exceed the pore size limit of the framework. Mesoporous silicates are attractive as hosts because they have offered expanded pore size ranges of up to and over 100 Å.[5−10] The extension of this class of materials to transition metal oxides with variable oxidation states[11−19] further expands the capabilities of mesoporous hosts by allowing electron transfer reactions to occur between the guest phase and the walls of the mesostructured lattice, thus allowing for systematic studies of nonstoichiometry on the physical properties of the composite.

In a recent report we showed that mesoporous niobium oxide (Nb-TMS1) can act as a potent stoichiometric electron acceptor.[20] While alkali metals are capable of reducing the framework by a total of one oxidation state without loss of the mesostruc-

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ture, weaker organometallic reductants such as cobaltocene leave low-dimensional mixed-oxidation-state phases within the pores of the structure.[21] These cobaltocene-reduced materials are superparamagnetic, a property normally associated with nanometer-sized grains of metals. In another report we showed that isolation of alkali fullerides in the mesopores of Nb-TMS1 was a convenient method to study the relationship between conductivity and oxidation state in one-dimensional fulleride nanostructures.[22] In a more recent study we showed that mixed-valent bis(benzene) chromium phases in the pores of Nb-TMS1 are highly conductive, suggesting that oxidation-state defects in metallocenes may lead to metallic behavior.[23]In order to further probe into the nature of low-dimensional bis-arene phases supported by mesoporous transition metal oxide hosts, in this report we synthesized related bis(benzene) vanadium composites and investigated their electronic properties. Since conductivity in solids is partially dependent on the Hubbard potential U ($I - A$) and its relation to the bandwidth W, it seemed plausible that, by going from the bis(benzene) chromium material with $2 - n$ electrons in the a_{1g} conduction band to the vanadium analogue with one less electron in this level, we might observe a change in conductivity through the channels due to a perturbation of the balance between U and W.[24] Further, since bis(benzene) vanadium is more easily oxidized than the Cr analogue, we expected a greater maximum dopant-to-niobium ratio in this vanadium-based composite, possibly leading to further increases in conductivity.

Experimental Section

Materials and Equipment. All chemicals unless otherwise stated were obtained from Aldrich. Samples of mesoporous niobium oxide (Nb-TMS1) were obtained from Alfa-Aesar and used without further purification. Trimethylsilyl chloride was obtained from Aldrich and distilled over calcium hydride. Nb-TMS1 samples were dried at 100 °C overnight under vacuum and then stirred with excess trimethylsilyl chloride in dry ether for 12 h under nitrogen. Bis(benzene) vanadium and the tetrachloroaluminate salt of the bis(benzene) vanadium cation were both prepared according to the literature.[25] Nitrogen adsorption and desorption data were collected on a Micromeritics ASAP 2010. X-ray diffraction (XRD) patterns (Cu Kα) were recorded in a sealed glass capillary on a Siemens D-500 $\theta - 2\theta$ diffractometer. All X-ray photoelectron spectroscopy (XPS) peaks were reference to the carbon C-(C,H) peak at 284.8 eV, and the data were obtained using a Physical Electronics PHI-5500 spectrometer using charge neutralization. Conductivity measurements were recorded on a Jandel four-point universal probe head combined with a Jandel resistivity unit. The equations used for calculating the resistivity were as follows. For pellets of <0.5 mm thickness,

$$\rho = \left(\frac{\pi}{\log n^2}\frac{V}{I}\right)t$$

was used. For pellets of >0.5 mm thickness, the following equation was used:

$$\rho = 2\pi(S)\frac{V}{I}$$

In these equations, ρ = resistivity; $\pi/\log n^2$ = sheet resistivity; V = voltage; I = current; t = thickness of the pellet; S = the spacing of the probes (0.1 cm).

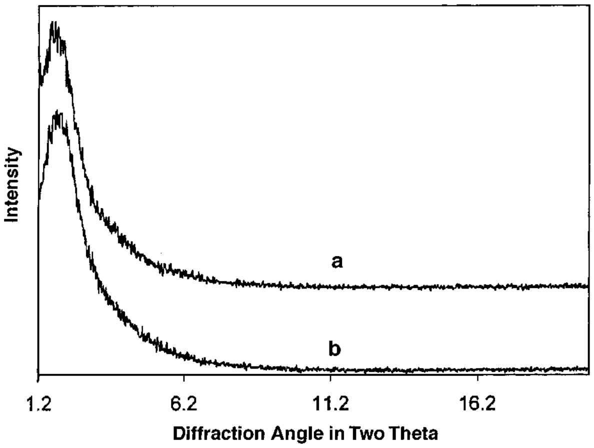

Figure 1. XRD of mesoporous niobium oxide (a) before and (b) after treatment with excess bis(benzene) vanadium.

The powder UV–visible spectra were collected on an Ocean Optics S2000 fiber optics spectrometer equipped with an Analytical Instrument Systems light source emitter with a tungsten halogen lamp and an Ocean Optics UV 0.4 mm, 2M reflection probe. The powder electron paramagnetic resonance (EPR) samples were prepared under vacuum and the data collected on a Bruker X-band ESP 300E EPR spectrometer. Magnetic measurements were conducted on a Quantum Design SQUID magnetometer MPMS system with a 5 T magnet. The solid-state NMR spectra were recorded on 270 MHz MAS NMR spectrometer at a spinning speed of 4.8 kHz without cross polarization. The Raman spectra were recorded on a Renishaw Ramascope using a Renishaw 780 nm diode laser system. All elemental analysis data (conducted under an inert atmosphere) were obtained from Galbraith Laboratories, 2323 Sycamore Drive, Knoxville, TN 37921-1700.

Synthesis. To a suspension of the Nb-TMS1 in dry benzene was added excess bis(benzene) vanadium calculated on the basis of metal percent as determined from elemental analysis. The mesoporous solid immediately went from a light fawn color to a deep gray-black (Nb-TMS1). After several days and additional stirring to ensure complete absorption of the organometallic, the reduced material was collected by suction filtration and washed several times with benzene. Once synthesized, the material was dried in vacuo at 10^{-3} Torr on a Schlenk line until all condensable volatiles had been removed. All other reduced oxides in this study were prepared in an analogous fashion.

Results and Discussion

When a sample of trimethylsilated Nb-TMS1[26] with an X-ray powder diffraction (XRD) peak centered at $d = 45$ Å, an HK pore size of 28 Å, a BET surface area of 580 m^2 g^{-1}, and a pore volume of 0.500 cm^3 g^{-1} was treated with excess bis(benzene) vanadium[25] in benzene over several days, a new black material was formed, collected by suction filtration, and dried in vacuo for 6 h to ensure complete removal of free solvent from the structure. Figure 1 shows the XRD peaks of the materials before and after treatment with bis(benzene) vanadium. The symmetric peak centered at 45 Å in the product demonstrates that this material fully retained its mesostructure on intercalation of the organometallic. Figure 2a shows the nitrogen adsorption and desorption isotherms of the materials from Figure 1b. The BET surface area of the treated sample dropped to 467 m^2 g^{-1} while the pore size and pore volume decreased to 25 Å and 0.363 cm^3 g^{-1}, respectively. Figure 2b shows the plots of incremental pore volume versus average pore diameter as calculated from the adsorption string of the isotherm. The

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(26) The starting material obtained from Alfa-Aesar after treatment with trimethylsilyl chloride gave 56.60% Nb and 5.39% C by weight. The material after treatment with 0.3 equiv of bis(benzene) vanadium gave values of 43.97% Nb, 9.13% C, and 7.64% V.

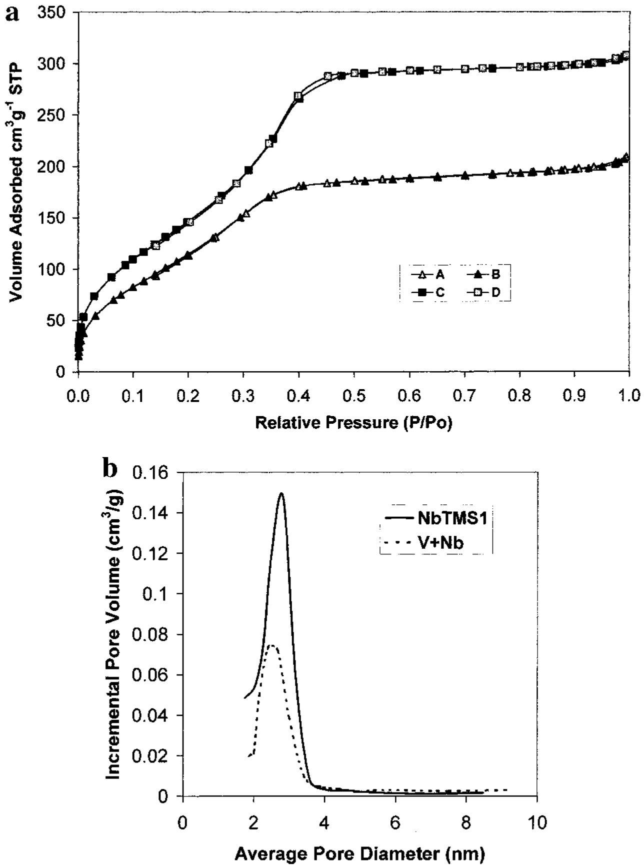

Figure 2. (a) Nitrogen adsorption (B, C) and desorption (A, D) isotherms of mesoporous niobium oxide before (C, D) and after (A, B) treatment with excess bis(benzene) vanadium. (b) Incremental HK pore volume vs pore diameter before (solid line) and after (dotted line) treatment with excess bis(benzene) vanadium.

retention of the XRD pattern and the same type of nitrogen adsorption/desorption isotherms with a decrease in pore size, pore volume, and surface area as compared to the starting materials are all consistent with occlusion of the pores of the mesostructure by the encapsulated organometallic. The decrease in pore size by even 3 Å and the same XRD *d* spacing after reduction suggests that the pore wall in the product is 3 Å thicker than that of the starting material. The elemental analysis[26] of this new material showed an increase in carbon from 5.39% in the starting material to 9.13% with 7.64% V as determined by inductively coupled plasma. The formula of this material can be calculated from these data as $Nb_{1.0}O_{4.8}V_{0.3}C_{1.6}H_{3.3}Si_{0.1}$ and was reproducible under the same preparation conditions within an acceptable range of error. The increase in carbon is consistent with partial retention of the structure of the bis(benzene) complex with some degradation to a surface vanadium species and free benzene. The V:Nb ratio in this material is 0.3:1, greater than the Cr:Nb ratio for the related bis(benzene) chromium intercalates (0.07:1) synthesized under identical conditions, presumably due to the greater capacity of the vanadium arene complex to act as an electron donor to the niobium oxide mesostructure, the electrochemical behavior of which has been discussed elsewhere.[27,28]

The UV−visible spectrum of this material shows a complex series of absorbancies. The peak at 240 nm has been observed previously and can readily be assigned to the Nb−O sp VB−CB transition.[20] The strong absorbances at 444 and 324 nm are due to free bis(benzene) vanadium,[29] while those at 479 and 340 nm are due to the corresponding cation on the basis of comparison to the UV spectrum of the tetrachloroaluminate salt. The absorbance at ca. 580 nm, corresponding to a band gap of 2.1 eV, appears in all reduced Nb-TMS1 species we have encountered to date and can be attributed to the transition from the dopant impurity band to the conduction band in the reduced mesoporous niobium oxide framework.[20] In this case the impurity band can best be described as V3d-Nb4d in character. These data confirm that bis(benzene) vanadium has been absorbed into the pore structure of the material and indicate that a portion of this species was oxidized by the niobium oxide framework as seen previously for the cobaltocene and bis(benzene) chromium intercalates.

The electron paramagnetic resonance (EPR) spectrum of this material is shown in Figure 3. This spectrum shows that two organometallic species of vanadium have been obtained. The eight lines that have axial symmetry of both **g** and ^{51}V hyperfine tensors with the following spin Hamiltonian parameters confirm the presence of bis(benzene) vanadium: $(g_{xx} = g_{yy} = g_{\perp} = 1.982)$:$(g_{zz} = g_{\parallel} = 2.002)$:$(A(xx) = A(yy) = 92.30G)$:$(A(zz) = 15.00G$. The extra peak ($g = 1.992$) between $m_I = \pm{}^1/_2$ is due to unstructured resonance associated with spin exchange in bis(benzene) vanadium,[29] providing further evidence that this species has aggregated in the pores. In addition to this resonance, there is a broad peak from 1000 to 2900 G providing evidence for the bis(benzene) vanadium cation, which displays a similar resonance in this region. This peak indicates very strong electron spin−spin interactions in the system. The resonance at 3369 G normally associated with the free electron in the walls of the reduced mesostructure is not discernible, possibly because it is obscured by the resonance due to the neutral bis(benzene) vanadium. The EPR data is thus consistent with the mixed-oxidation-state formation of this material where the low-dimensional molecular phase of bis(benzene) vanadium and its corresponding cation reside in the pores of a partially reduced niobium oxide framework.

The ^{1}H-MAS NMR spectrum of this material exhibits a broad peak at 7.0 ppm which can be assigned to the protons associated with neutral bis(benzene) vanadium in the sample. This resonance is comparable to that at 6.8 ppm obtained from the ^{1}H-MAS NMR spectrum of pure bis(benzene) vanadium. The small chemical shift to the lower magnetic field is possibly due to the magnetic shielding of the reduced paramagnetic mesoporous framework. There is a second resonance at 13.4 ppm in the sample which can be assigned to the arene protons of the bis(benzene) vanadium cation according to the ^{1}H-MAS NMR spectrum of the tetrachloroaluminate salt. A peak due to the trimethylsilyl protons at 0.1 ppm was also observed in the material and compares closely in shift to the same resonance in unreduced mesoporous niobium oxide. ^{51}V-MAS NMR measurements were also attempted; however, no peaks were observed. This is not surprising, as ^{51}V NMR signals are usually too broad to observe in paramagnetic samples. Raman spectroscopic measurements were also conducted on these materials to further probe into the nature of the occluded species in the pores. The strong resonance band at 265.9 cm^{-1} due to the symmetric bz−V−bz stretching mode in the pure bis(benzene) vanadium was too week to be resolved in the reduced samples. This can be explained by either low loading levels or quantum

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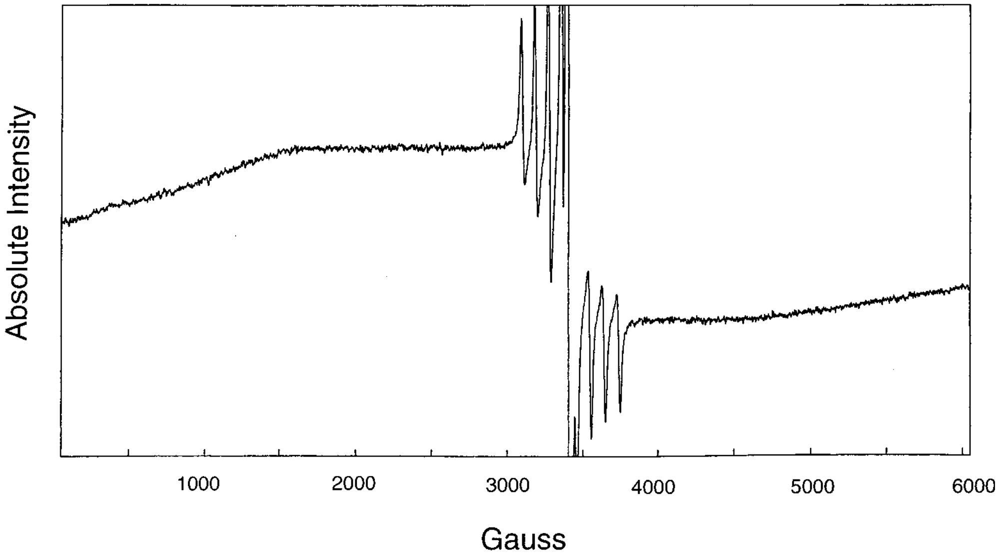

Figure 3. Powder EPR spectrum of mesoporous niobium oxide treated with excess bis(benzene) vanadium.

confinement effects within the reduced niobium oxide framework leading to inactivity of this mode. The lack of this bz−V−bz stretching mode of bis(benzene) chromium was also noted in the Raman spectra of bis(benzene) chromium mesoporous niobium oxide composites.

In order to further probe into the electronic structure of this new material, X-ray photoelectron spectroscopy (XPS) studies were conducted. This surface technique provides a useful picture of the composition of the material, since the extremely high surface areas, large pores, and thin walls (ca. 3−5 monolayers) possessed by the material ensure that the vast majority of sites are located on or just below the inner surface of the pore channels in the material. Also, owing to the facile diffusion properties afforded by the mesopores it is unlikely that reduction only occurs on the outside of the mesoporous particles. Figure 4a shows the Nb 3d region of the starting material and the reduced material with the $^5/_2$ and $^3/_2$ peaks in clear evidence. The position of the $^5/_2$ peak in the reduced species at 206.0 eV is consistent with partial reduction of the Nb oxide framework.[20] In previous work we showed that reduction of the niobium oxide framework led to a decrease in peak position with dopant loading level.[20] These peaks are also much broader than those in the starting material, as is the O 1s peak, providing further evidence for reduction of the Nb framework by bis(benzene) vanadium. Simulation of the $^5/_2$ and $^3/_2$ peaks in the spectrum of the reduced material reveals new peaks for reduced niobium species at 206.0 and 208.9 eV, respectively. Figure 4b shows the V 2p $^3/_2$,$^1/_2$ region showing a series of emissions which can be simulated from the XPS spectra of the pure compounds to fit a mixture of neutral bis(benzene) vanadium (520.5 and 513.3 eV), the corresponding cation (522.1 and 514.5 eV), and a V(II) species (523.2 and 515.6 eV). The presence of V(II) in this system[30] is not unexpected in light of the lower-than-expected carbon values in the elemental analysis and the well-documented tendency of the bis(benzene) vanadium cation to disproportionate into the neutral species and a V(II) species, in this case an oxide.[31] Figure 4c shows the region near the Fermi level with a rough distance to the Fermi level of 3.3 eV for the metal−oxygen sp valence emission, comparable to that observed in related materials, and a small peak near the Fermi level that can be assigned to the V3d emission.[31]

Figure 5a shows the superconducting quantum interference device (SQUID) magnetometer plot of magnetic susceptibility versus temperature for the composite. The hysteresis in this curve can be attributed to the broad distribution of particle sizes in the mesoporous oxide, which gives a wide range of roughly spherical particles from 50 to 1000 nm.[28] The slight transition in the ZFC branch of the plot indicates some degree of superparamagnetic or spin glass behavior, although this contribution is clearly much weaker than that observed for related superparamagnetic cobaltocene intercalates.[21] In a recent report we discussed a family of nickelocene composites of mesoporous niobium oxide which show an interesting dopant-dependent paramagnetic to superparamagnetic to spin glass transition.[32] Figure 5b shows the variation of inverse molar magnetic susceptibility with temperature over the temperature range from 6 to 100 K, demonstrating that this material obeys the Curie−Weiss law where $\chi_m = C/(T - \theta)$. From this plot, the Curie constant C can be calculated as 3.41 emu mol^{-1} K and the Weiss constant θ is -22.39 K, indicating that there are subtle antiferromagnetic interactions in the material, which tends to support spin glass rather than superparamagnetic behavior in this system. The effective magnetic moment μ_{eff} can be calculated as 1.65 from the equation $C = N/\mu_B{}^2\mu_{\text{eff}}{}^2/3\kappa$. The B vs H plots at 5 and 100 K of this V composite show a linear progression, typical only of paramagnetic species, indicating that paramagnetism dominates the behavior of this system.

Electron transport properties in these bis(benzene) vanadium intercalates was measured by the four-point method and revealed reproducible values in the range from 1 to 5.0 × 10^{-4} ohm^{-1} cm^{-1}, almost 50 times greater than that observed in the related Cr species. Since the reduced framework of Nb-TMS1 has been previously shown to be insulating,[20] these materials are convenient hosts for the study of conductivity in one-dimensional molecular phases within the pores, as all conductivity must therefore arise from interactions between the encapsulated species and not the walls of the structure. Unpublished results from our group showed that unreduced and Li-reduced mesoporous niobium oxides are ion insulators, thus ruling out any contribution to conductivity from proton or ion transport. It is

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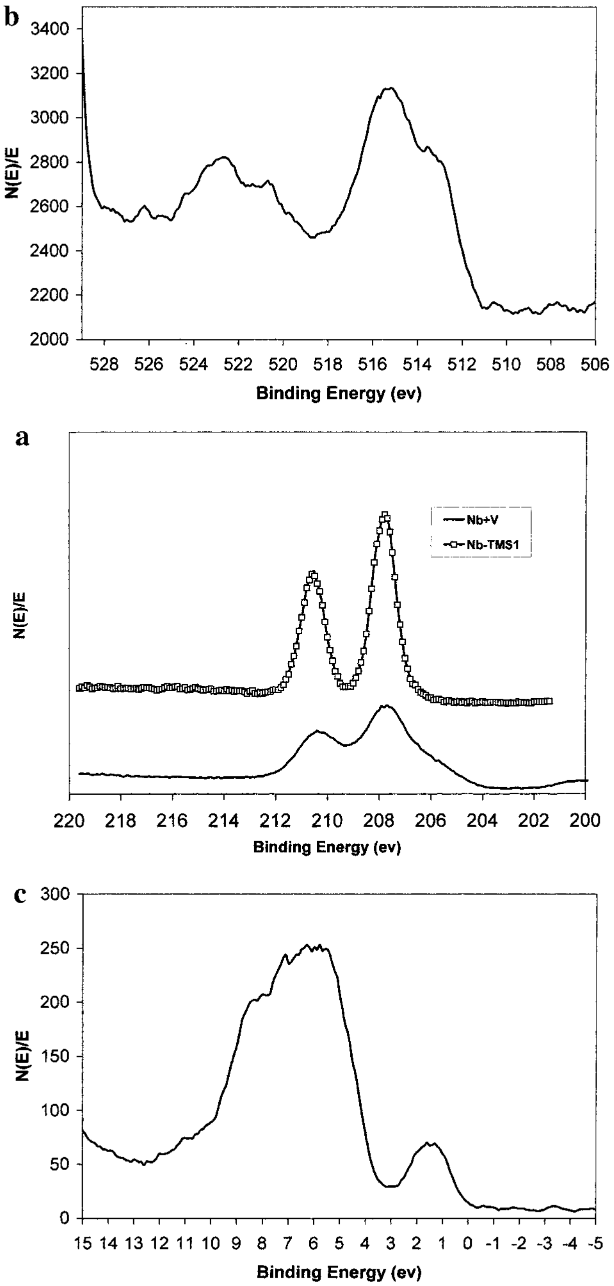

Figure 4. XPS spectrum of mesoporous niobium oxide treated with excess bis(benzene) vanadium showing (a) the Nb 3d region; (b) the V 2p region; and (c) the region near the Fermi level.

also unlikely that surface protons would be present, since acid is readily reduced to H_2 by bis(benzene) vanadium. In order to gauge the contribution made by the low-dimensional molecular phase in the pores of the material as opposed to that deposited on the external surface of the material, amorphous niobium oxide treated with trimethylsilyl chloride with a BET surface area of 91 m^2 g^{-1} was treated with bis(benzene) vanadium under the same conditions to yield dark gray composites with conductivities of less than 10^{-7} ohm^{-1} cm^{-1}. XPS studies of this material showed the expected slight reduction of the Nb oxide. These data suggest that the dopant phase deposited on the outer surface does not contribute to the overall conductivity of the mesoporous composites to any significant extent. This is not entirely surprising since the ratio of outer surface area to inner surface area due to the pores is less than 1:250 on the basis of the nitrogen adsorption data. The role of V(II) in this system, present as an oxide dopant in or on the surface of the walls of the mesostructure, in the conductivity is not completely understood. However, vanadium oxide doped (1−20 mol % V) Nb-TMS1 samples have been studied in our group and have only shown insulating properties (less than 10^{-8} ohm^{-1} cm^{-1}).[33] These materials were reduced with alkali metals to form low-valent V species in the walls; however, this led only to insulating behavior. The as-synthesized bis(benzene) vanadium composites were also oxidized in air at 100 °C for 24 h to ensure complete degradation of the organometallic and then reduced with K-naphthalene. These materials were also insulating. All of these experiments suggest that conductivity in this V system arises only from the presence of a mixed-oxidation-state organometallic phase in the pores of the material. Since the kinetic diameter of bis(arene) complexes is ca. 10 Å and the pore diameter of the mesoporous niobium oxide is 28 Å, it is reasonable to conclude that the pores can accommodate one or two organometallic units across the pore diameter.

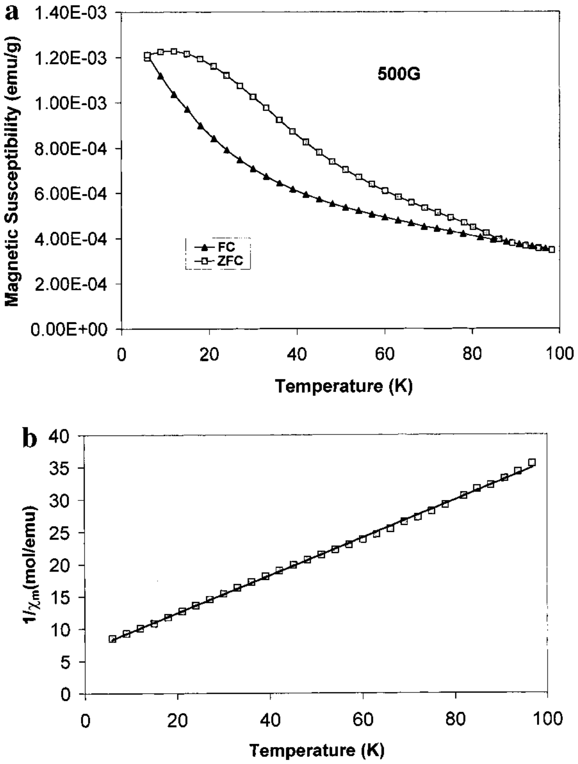

Figure 5. (a) SQUID magnetometer plot of magnetic susceptibility versus temperature for a sample of mesoporous niobium oxide treated with excess bis(benzene) vanadium showing the field-cooled (FC) and zero-field-cooled (ZFC) branches of the plot. (b) Plot of the variation of inverse molar magnetic susceptibility with temperature at a magnetic field of 500G for sample in panel a.

Understanding the mechanism of conductivity in these materials is complicated by the fact that the ground-state configuration of bis(benzene) vanadium cation is $e_{2g}{}^{3}a_{1g}{}^{1}$, suggesting that the conduction band in the vanadium composite has mixed a_{1g}/e_{2g} character.[34] In molecular metals such as TCNQ salts, a change in metallic to insulating behavior is observed in going from TCNQ/TTF with 0.59 electron in the π^* conduction band to TCNQ/K with 1 electron in the conduction band.[35] In related mesoporous niobium oxide−alkali fulleride materials we showed that the decreased T_{1u} band filling in one-dimensional alkali fulleride phases within the mesopores of Nb-TMS1 altered the physical behavior of the composite from insulating at $n =$

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3 to metallic at $n = 0.6$. The reasons for the increase in conductivity in these bis(benzene) vanadium materials with respect to the Cr analogues are not clear but according to our model may be related to the decreased number of electrons in the a_g conduction band of this species due to a change from Cr d^6 (a_g^{2-n}) to V d^5 where $n =$ the number of electrons transferred from the organometallic phase to the walls of the structure. Other factors that may also be at play are the difference in potential of the V(0)/V(I) and Cr(0)/Cr(I) redox couples as well as the more facile oxidation of the vanadium species leading to a higher loading level within the mesopores which would in turn lead to a more continuous spacing of the individual molecules within the structure. This greater homogeneity in the structure could also lead to improved conductivity within the channels.

Metallic conductivity in solids depends on Hubbard potential ($U = I - A$), where I is the ionization potential and A is the electron affinity of the charge-carrying species, and the bandwidth (W). If W is greater than U, the material will be conducting. If it is not, then the material will be insulating. Since W is difficult to calculate in an amorphous system, it is also meaningful to use pure metal bandwidth (W) in this system. The Hubbard potential can be estimated by considering the I values of 5.72 eV[36] and 5.40 eV[37] for bis(benzene) vanadium and bis(benzene) chromium, respectively, along with A values for the corresponding cationic species. Although the A values for their cations are not available in the literature, they can be estimated from the A values of bis(benzene) vanadium(0) and bis(benzene) chromium(0), and bis(cyclopentadienyl) vanadium(II) and bis(cyclopentadienyl) chromium(II). The A values for bis(benzene) vanadium and bis(cyclopentadienyl) vanadium are -0.29 eV[38] and 0.68 eV,[39] respectively. We can use half the difference $[(0.68\text{ eV} + 0.29\text{ eV})/2 - 0.29\text{ eV} = 0.195\text{ eV}]$ between them as the A value for the bis(benzene) vanadium(I) cation. The A values for bis(benzene) chromium and bis(cyclopentadienyl) chromium are -0.76 eV[40] and 0.88 eV,[39] respectively, and the same calculation as described above for half the difference gives 0.06 eV as the A value for the bis(benzene) chromium(I) cation. Therefore, the Hubbard potential U for the vanadium system will be 5.525 eV ($=5.72\text{ eV} - 0.195\text{ eV}$) and for the chromium system will be 5.34 eV ($=5.40\text{ eV} - 0.06\text{ eV}$). From this analysis and comparison to the estimated maxium value for the bandwidth W of 6.77 eV for vanadium and 6.56 eV for chromium, it would appear that conductivity in both systems should be favorable according to this model.

In order to more fully explore the effect of electronic configuration on conductivity in these materials, we treated Nb-TMS1 with bis-1,3,5-tri-*tert*-butylbenzene yttrium[41] under the assumption that the d^3 species may give different behavior due to the smaller number of valence electrons per mole of dopant. Comparison of this new material to the V analogue is not simple, however, since this bis-arene species does not have electrons in the a_g level, but only in the lower doubly degenerate e_g level. The material was prepared by stirring trimethylsilated Nb-TMS1 in benzene with the Y precursor. The black color of the reduced material indicated that reduction of the niobium framework occurred as expected by the strongly reducing character of this species. The XRD showed a peak at $d = 45$ Å, and the nitrogen adsorption data showed a drop in surface area to 423 $m^2\ g^{-1}$, consistent with retention of the mesostructure and partial filling of the pores of the niobium oxide framework. Elemental analysis showed that while 2.65% Y had been absorbed, the carbon value did not increase significantly with respect to the starting material. This is consistent with the organometallic acting as a source of Y in much the same way that Na-naphthalene acted as a source of Na in previously studied reduced mesoporous niobium oxide materials. Like this Na-reduced material, the Y-doped composite was insulating, suggesting that this material is also subject to Anderson localization effects. Thus, the Y composite is best described as a direct analogue of the Na-reduced materials with a Y center replacing three Na centers in or on the wall of the reduced mesostructure, and thus it cannot be directly compared to the V and Cr materials, which have low-dimensional organometallic phases occluding the pores.

Conclusion

In conclusion we have synthesized and characterized a new bis(benzene) vanadium intercalate of Nb-TMS1 in which the mixed oxidation state of the vanadium phase is most likely responsible for the electronic conduction within the mesopores of the material. This conductivity appears to arise from the formation of a molecular phase in the pores of the material and the introduction of charge-carrying holes in the e_{2g} band of this phase; however, a small contribution from the surface conductivity of V(II) species may also be important. The higher conductivity of these materials compared to related bis(benzene) chromium intercalates could be attributed to a decrease in the number of electrons in the conduction band and formation of the mixed-oxidation-state molecular phase as well as the higher percentage of the vanadium species in the pores compared to the Cr material. Currently we are studying the subtle relationships between electronic conductivity in these materials and loading level, reduction potential, electronic configuration, and ratio of oxidized species to reduced species within the pores as well as orientation and possibly interatomic spacings between the individual molecules as determined by ^{2}H-MAS NMR on ^{2}H-labeled organometallics.

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