Superparamagnetic and spin glass behavior in mesoporous niobium oxide bis(cyclopentadienyl)nickel composites

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Herein we report the synthesis and characterization of a new family of mesoporous niobium oxide bis(cyclopentadienyl)nickel composites which exhibit superparamagnetic or spin glass behavior depending on the different loading levels of the organometallic in the pores. XRD and nitrogen adsorption studies confirm the retention of the mesostructure in these new materials upon introduction of the guest species. The Nb 3d region of the XPS provides evidence for the slight reduction of the Nb(v) oxide walls while the Ni 2p region shows the presence of both neutral and cationic bis-cyclopentadienyl nickel species with peaks at 856.3 eV and 861.9 eV respectively, as well as two more highly oxidized species at 865.5 eV and 867.3 eV. The presence of neutral and cationic bis(cyclopentadienyl)nickel is further confirmed by EPR. SQUID magnetic measurements show superparamagnetic behavior for the material with a Ni : Nb ratio of 0.07 : 1, while at a ratio of 0.1 : 1 the material shows spin glass behavior, a phenomenon normally associated with amorphous metal alloys. The difference in magnetic behavior is rationalized by an increased density of unpaired spins in the pore structure.

Introduction

Recently we reported that mesoporous Nb oxide[1,2] can act as a stoichiometric electron acceptor while fully retaining its mesostructure,[3] a property not possessed by MCM-41 and other mesoporous silicates,[4–7] due to the variable oxidation state capacity of the transition metal oxide framework.[8–16] This capacity not only opens the doorway for the synthesis of mesoporous fast ion conduction channels and design of catalytic processes where the electronic activity of the porous support material is important, but it also allows for the synthesis and encapsulation of mixed oxidation state nanometer-sized guest phases within the pores.[17,18] While grains of nanostructured materials often possess different properties not observed in the bulk phase, the introduction of non-stoichiometric defects in a material can lead to new and unusual physical behavior. While reduction of the niobium oxide host matrix with alkali metals leads to reduced mesostructured Nb(iv) materials which are insulating and paramagnetic,[3,19] reaction of mesoporous niobium oxide with a variety of highly-reducing organometallic sandwich complexes has led to a new family of mesostructured composites with mixed oxidation state molecular phases within the pores. The bis(benzene)chromium and bis(benzene)vanadium composites are paramagnetic and conducting due to metallic behavior in the one-dimensional organometallic phase within the pore channels,[20,21] while the cobaltocene materials are superparamagnetic, providing the first example of this interesting magnetic phenomenon, normally associated with fine metallic and oxide particles, in a molecular ensemble.[22,23] In another study, impregnation of the niobium oxide pore structure with alkali fullerides led to the formation of one-dimensional fulleride nanowires with electronic properties strongly contrasting with those of the bulk materials.[24,25] In order to more fully explore the reasons behind the diverse physical behavior observed on intercalating different organometallic species within the pores, we herein report a study on the magnetic and electronic properties of mesoporous niobium oxide bis(cyclopentadienyl)nickel composites. Since there are two unpaired electrons in bis(cyclopentadienyl)nickel, as opposed to only one in cobaltocene, we expected these composites to possess different magnetic and electronic properties than the cobaltocene analogues.

Experimental

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 stirred with excess trimethylsilyl chloride in dry ether for 4–6 h under nitrogen and then dried at 100 °C overnight under vacuum. Bis(cyclopentadienyl)nickel was obtained from Aldrich and used without further purification. Nitrogen adsorption data were collected on a Micromeritics ASAP 2010. X-Ray diffraction (XRD) patterns (CuKα) were recorded in a sealed glass capillary on a Siemens D-500 θ–2θ diffractometer. All X-ray photoelectron spectroscopy (XPS) peaks were referenced to the carbon C–(C,H) peak at 284.8 eV and the data were obtained using a Physical Electronics PHI-5500 using charge neutralization. The conductivity measurements were recorded on a Jandel 4 point universal probe head combined with a Jandel resistivity unit. The equations used for calculating the resistivity were as follows: for pellets of <0.1 mm thickness $\rho = [\{\pi/(\log n^2)\}(V/I)]t$, and for pellets of >0.5 mm $\rho = 2\pi(S)[V/I]$, where 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). 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, 2 M reflection probe. All EPR spectra were recorded at the temperature of liquid nitrogen on an X-band Bruker ESP 300E spectrometer equipped with a

microwave counter, an NMR magnetometer and an electromagnet capable of providing a magnetic field range from 50 G to 15 kG. The measurement conditions for the spectra were microwave power 20.0 mW, microwave frequency 9.50 GHz, modulation frequency 100.00 kHz, modulation amplitude 3.83 G, and receiver gain 1.00×10^5. The powder samples used in the experimental measurements were sealed under vacuum in quartz tubes. Magnetic measurements were conducted on a Quantum Design SQUID magnetometer MPMS system with a 5 T magnet. All elemental analysis data were obtained from Galbraith Laboratories, 2323 Sycamore Drive, Knoxville, TN 37921-1700, USA.

Synthesis

To a suspension of Nb-TMS1 in benzene was added 0.5 equivalents of bis(cyclopentadienyl)nickel calculated on the basis of the percentage of niobium as determined from the elemental analysis data. The solution gradually lightened, indicating absorption of the organometallic, and the mesoporous solid went from a light faun color to a deep green-yellow. After several days of additional stirring to ensure complete absorption of the bis(cyclopentadienyl)nickel, the reduced material was collected by suction filtration and washed several times with benzene. Once synthesized, all materials were dried *in vacuo* at 10^{-3} Torr on a Schlenk line until the vacuum gauge showed that all condensable volatiles had been removed. Elemental analysis of the bis(cyclopentadienyl)nickel composites synthesized are given below. Nb-TMS1 with an HK pore size of 22 Å, $d = 32$ Å treated with NiCp$_2$: 8.01% C, 1.53% H, 0.01% N, 1.48% Si, 48.80 Nb, 2.08% Ni. The same parent sample treated with excess Cp$_2$Ni: 9.92% C, 1.71% H, 0.01% N, 1.35% Si, 48.10 Nb, 2.96% Ni.

Results and discussion

Treatment of a sample of trimethylsilated mesoporous niobium oxide with a BET surface area of 947 m^2 g^{-1}, an HK pore size maximum at 22 Å, and an X-ray powder diffraction (XRD) pattern with a single peak at $d = 32$ Å with excess bis(cyclopentadienyl)nickel in benzene at ambient temperature for three days gave a new green material which may be isolated by suction filtration and repeated washing with benzene followed by drying *in vacuo* at 10^{-3} Torr. The XRD pattern of this new material is shown in Fig. 1 and displays a peak at $d = 32$ Å, confirming retention of the mesostructure. The nitrogen adsorption–desorption isotherms of the starting material and bis(cyclopentadienyl)nickel composite are shown in Fig. 2. The BET surface area of the composite was 693 m^2 g^{-1} and an HK pore size maximum at 21 Å. The pore volume of this material dropped from 0.59 cm^3 g^{-1} to 0.39 cm^3 g^{-1}. All of these data confirm retention of the mesostructure with partial occlusion of the pores with an organometallic nickel species. While
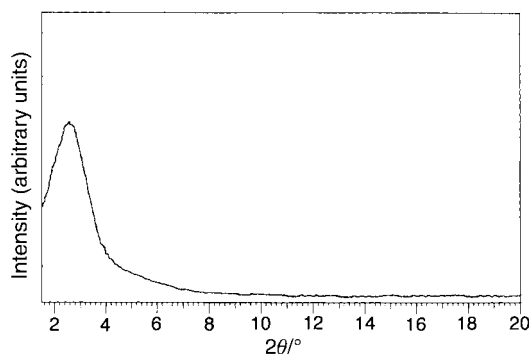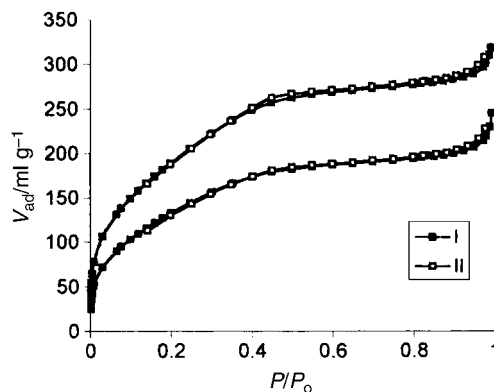

Fig. 2 Nitrogen adsorption (I) and desorption (II) isotherms of mesoporous niobium oxide before (upper) and after (lower) treatment with bis(cyclopentadienyl)nickel.

mesoporous niobium oxide–cobaltocene composites are gray to black in color, the green color of the bis(cyclopentadienyl)nickel material suggests that different chemistry may be occurring in this system. In contrast to the chemistry of cobaltocene, which is relatively straightforward due to the strong propensity of this species to act as a one-electron donor to form the thermally very stable 18-electron cation, the chemistry of bis(cyclopentadienyl)nickel can involve one[26] or two[27] electron transfer as well as further complications with possible protonation of the ring and loss of neutral cyclopentadiene[28] or ligand substitution by donor ligands to remove the cyclopentadiene anion.[29]

The elemental analysis of this new bis(cyclopentadienyl) composite gave values of 8.01% C, 1.53% H, 48.80% Nb, 1.48% Si, and 2.08% Ni. While the value of 2.08% Ni suggests an increase in C of roughly 4.3% from the 4.46% present in the starting material due to the trimethylsilyl groups, the actual increase in C of only 3.65% indicates that a small loss of organic has occurred. The UV-visible reflectance spectrum of this new material showed a broad range of absorbances from 250 nm to 800 nm with peaks at 590 nm, 434 nm, and 339 nm corresponding to the neutral Ni species and a peak at 306 nm which can be assigned to the cation.[26] Other weak absorbances present at 294 nm and 418 nm suggest the presence of other unidentified Ni species. The presence of the absorbance at 306 nm confirms that some electron transfer from the organometallic has occurred. Conductivity measurements of this material showed that like the alkali-metal reduced and cobaltocene-reduced mesoporous niobium oxide composites, this material is an insulator. While early-metal sandwich compounds such as bis(benzene)vanadium, bis(benzene)chromium, and bis(cyclopentadienyl)vanadium form mixed-valent molecular wires within the pore structure,[20,21] it appears that composites of late-metal sandwich compounds are insulating. The reason for this is still under investigation, but may be related to the relative orbital energies and electron configurations of the mixed-valent species present in the pore structure.

Fig. 3 shows the Ni 2p$_{3/2}$ region of the X-ray photoelectron (XPS) spectrum of the nickel-containing mesoporous composite. Apart from peaks at 856.3 eV and 861.9 eV corresponding to neutral and cationic bis(cyclopentadienyl)nickel,[30] there are small peaks at 865.5 eV and 867.3 eV, due to nickel species in a higher oxidation state. The integrated intensity ratios of these four peaks were calculated as 10 : 6 : 2 : 1 respectively. Although electrochemical data suggests the existence of the Ni(IV) dication,[27] it has never been isolated and structurally characterized. The peaks at higher energy may also be due to a decomposition product, such as a carbide or higher oxide, but are more likely due to nickel species in higher oxidation states that have lost a cyclopentadiene ring due to residual protons on the walls of the mesostructure. This would certainly account for
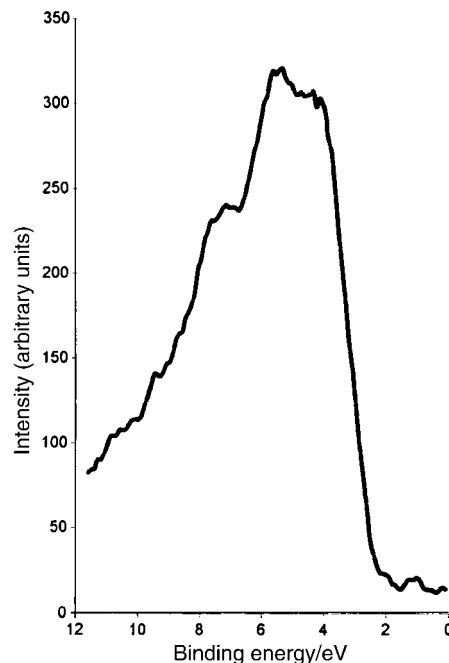

Fig. 1 XRD of mesoporous niobium oxide after treatment with bis(cyclopentadienyl)nickel.
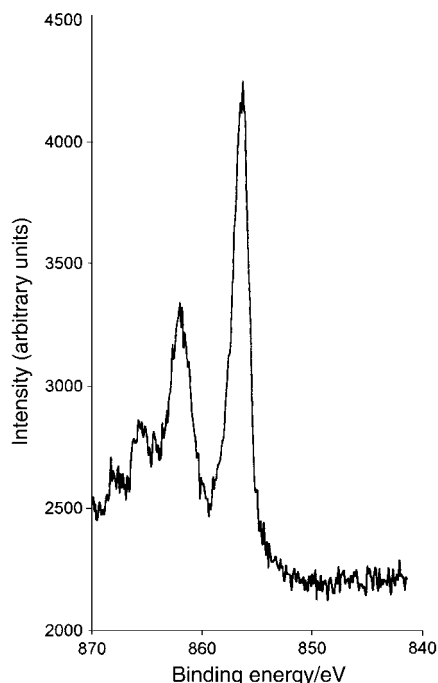
Fig. 3 Ni 2p$_{3/2}$ region of the XPS spectrum of mesoporous niobium oxide treated with bis(cyclopentadienyl)nickel.

the lower-than-expected carbon values. The Nb 3d region of the XPS (Fig. 4) shows peaks at 210.6 eV and 207.8 eV for the 3/2 and 5/2 peaks[3] demonstrating that the walls of the mesostructure are only slightly reduced in this material compared to the starting material which shows emissions at 210.8 eV and 208.0 eV. These data are consistent with a small degree of electron transfer into the walls of the mesostructure and formation of the bis(cyclopentadienyl)nickel cation and other more highly oxidized species. The valence region near the Fermi level (Fig. 5) shows a broad and complex hump for the Nb–O sp valence emission with a tail that ends at roughly 3.0 eV, consistent with other mesoporous niobium oxide
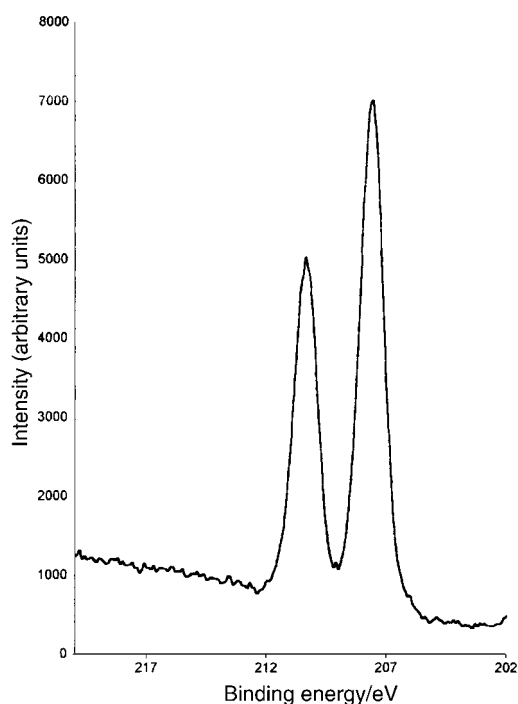
Fig. 4 The Nb 3d region of the XPS spectrum of a sample of mesoporous niobium oxide treated with bis(cyclopentadienyl)nickel.


Fig. 5 The region near the Fermi level of the XPS spectrum of a sample of mesoporous niobium oxide treated with bis(cyclopentadienyl)nickel.

composites studied in which an impurity band model seems most appropriate to describe the electronic structure.[3] Specific assignments of the shoulders and detailed peak convolution are difficult due to the high energy nature of XPS spectroscopy and the subtle electronic effects at play near the Fermi level. The absense of any significant emission near the Fermi level, however, is consistent with the insulating nature of this material.

The presence of paramagnetic neutral bis(cyclopentadienyl)-nickel (2.89 μ_B) and the corresponding cation (1.76 μ_B)[28] in the pore structure suggests that this material may have unusual magnetic properties. The electron paramagnetic resonance (EPR) spectrum of this material is shown in Fig. 6. The broad peak at 3054 G ($g = 2.22$) and the sharp peak at 3389 G ($g = 2.00$) provides further evidence for bis(cyclopentadienyl)-nickel in this material. The broad line is due to the superposition of the transition $|-1> \leftrightarrow |0>$ and $|0> \leftrightarrow |+1>$ and the sharp line is due to $|-1> \leftrightarrow |+1>$.[31] The much broader peak, which covers a large area of low field, can be assigned to the bis(cyclopentadienyl)nickel cation and illustrates very strong spin–spin interactions in the system. While reduced mesoporous oxides often show a peak for the free electron in the wall at 3369 G, this region is obscured by the large resonance at 3389 G and thus confirmation of this peak is difficult.

SQUID magnetic measurements were conducted to further
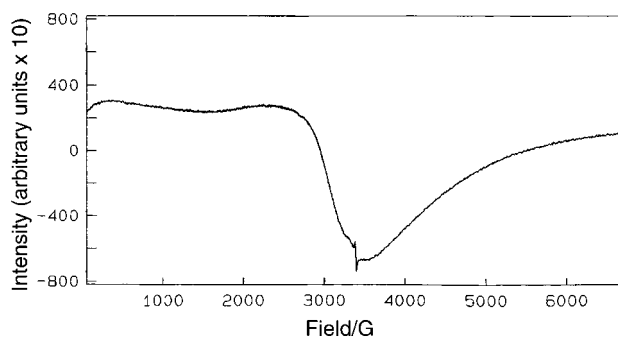
Fig. 6 Powder EPR spectrum of mesoporous niobium oxide treated with bis(cyclopentadienyl)nickel.
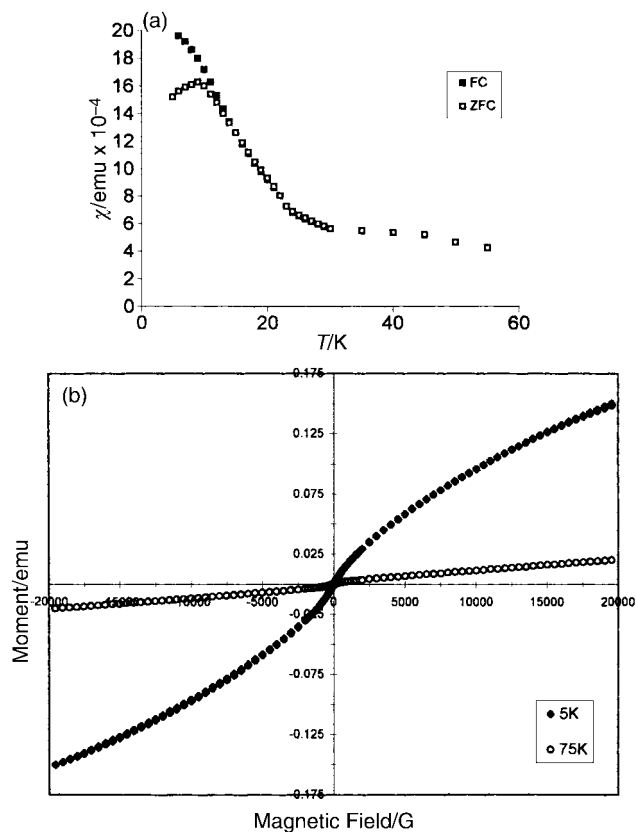
Fig. 8 SQUID magnetometer plot of magnetic susceptibility *versus* temperature for mesoporous niobium oxide with excess bis(cyclopentadienyl)nickel showing ZFC and FC branches of the plot.

Fig. 7 a) SQUID magnetometer plot of magnetic susceptibility *versus* temperature for a sample of mesoporous niobium oxide treated with bis(cyclopentadienyl)nickel showing the field cooled (FC) and zero field cooled (ZFC) branches of the plot. b) SQUID magnetometer plot of *B vs. H* for the sample from a).

explore the magnetic behavior of this new composite. The *M vs. T* plot measured at 500 G is shown in Fig. 7a and provides evidence for superparamagnetism, a phenomenon common in nanostructured metals and ferrofluids which arises from small domains of locally ordered spins.[32] The *M vs. T* plot of a superparamagnetic material shows a cusp at a blocking temperature (T_b) of 8 K. At 12 K the zero field cooled (ZFC) and field cooled (FC) branches bifurcate.[32] The *B vs. H* plot for this material run at 5 K and 75 K is shown in Fig. 7b. The absence of hysteresis and lack of a coercive field demonstrated in this plot are further hallmarks of superparamagnetic behavior. This has previously been observed in related cobaltocene composites of mesoporous niobium oxide and was attributed to mixed oxidation state cobaltocene–cobaltocenium grains in the pores of the material.[23] Detailed studies of this material showed a strong dependence of superparamagnetism, a property previously only observed in metals and ferrofluids, on the amount of cobaltocene, and hence the concentration of unpaired spins, within the pores of the mesoporous niobium oxide framework. The Co : Nb ratio was *ca.* 0.5 : 1 in this system, with samples possessing lower ratios of organometallic displaying only paramagnetic properties. Interestingly, the Ni-based composites in this study have Ni : Nb ratios of 0.07 : 1. This lower level of organometallic in the pores can be rationalized by the greater reduction potential of cobaltocene (0.94 V) with respect to bis(cyclopentadienyl)-nickel (0.09 V). Previously we showed that the level of absorption of guest species into mesoporous oxides was strongly dependent on the degree of electron transfer between the guest and the inorganic walls of the mesostructure.[23] The fact that the Ni composites show superparamagnetism at lower Ni levels can be explained by the greater number of unpaired electrons in these materials per mole of dopant. The ground
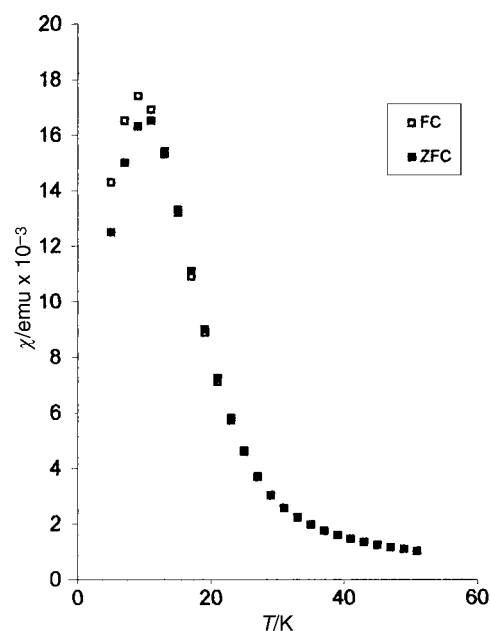
state of bis(cyclopentadienyl)nickel is a triplet, as compared to the doublet ground state of cobaltocene, while the ground state of the bis(cyclopentadienyl)nickel cation is a doublet and cobaltocenium a singlet. Thus, the onset of superparamagnetism in the Ni system can occur at lower concentrations of the organometallic dopant.

In order to investigate the dependence of loading on magnetic behavior, we investigated bis(cyclopentadienyl)nickel composites with higher levels of nickel in the pores. Hence, we synthesized a material with more bis(cyclopentadienyl)nickel by stirring the mesoporous material for ten days in a concentrated solution of bis(cyclopentadienyl)nickel and confirmed the retention of the mesostructure by XRD and nitrogen adsorption. The elemental analysis of this material showed an increase in Ni content from 2.08% to 2.96%, giving a Ni : Nb ratio of 0.1 : 1. The Ni $2p_{3/2}$ region of the XPS showed the same peaks as observed in Fig. 3, however the ratio of these emissions changed to 14 : 6 : 2 : 1 from 10 : 6 : 2 : 1, demonstrating that most of the extra bis(cyclopentadienyl)nickel was in the neutral form. The Nb 3d region and the valence region near the Fermi level are virtually identical to those of the material with a lower loading level shown in Figs. 4 and 5. The SQUID *M vs. T* plot in Fig. 8 shows a cusp in the ZC and ZFC branches of the plot, however below this temperature there is no bifurcation between these two branches, suggesting that this material is a spin glass, a magnetic phenomenon associated with amorphous metals. A cusp in the ZFC and FC curves in addition to the irreversibility of the FC susceptibility are footprints of the spin glass state where the cusp occurs at a freezing temperature (T_f) below which all spins are "frozen" into a particular orientation.[33,34] The fact that the FC and ZF cooled branches do not entirely overlap has been observed before and explained by cluster glass state or micromagnetic behavior, a common phenomenon in materials with a large concentration (*ca.* 10%) of magnetic species.[35] The reason superparamagnetism is observed in the system with lower loading while the material with higher loading is a spin glass is not fully understood, however very subtle increases in concentration of magnetically active species are known to bring about transitions from superparamagnetic to spin glass behavior.[33] This has been observed previously in a system of

amorphous Pd–Ni–Fe–P alloys,[34] where materials with higher levels of Fe, the dominant magnetic species, are spin glasses, while those with lower Fe levels are superparamagnetic or paramagnetic. The loading levels of the Ni in this system are significantly less than in the cobaltocene system, but the presence of two magnetically active species in the pores as opposed to only one more than makes up for this lower concentration of dopant. This is certainly consistent with the maximum magnetic moment in the plot in Fig. 8 (18×10^{-3} emu) being more than ten times greater than that in Fig. 7a (16×10^{-4} emu).

Conclusion

In conclusion, we have synthesized a new family of mesoporous niobium oxide–bis(cyclopentadienyl)nickel composites which exhibit either superparamagnetic or spin glass behavior depending on the loading level of the bis(cyclopentadienyl)-nickel in the pores. This is the first example of spin glass behavior in a mesoporous material and studies are ongoing to further investigate the reasons for this unusual physical behavior. In contrast to mesoporous niobium oxide–bis(benzene)chromium, bis(benzene)vanadium, and potassium fulleride composites, where mixed oxidation state one-dimensional molecular nanowires are invoked to explain the metallic or semiconducting behavior, the bis(cyclopentadienyl)nickel materials were insulating. The impregnation of mesoporous transition metal oxides with highly reducing organometallic species continues to be an area of great interest.

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