TRANSPARENT MONOLITHIC METAL ION CONTAINING NANOPHASE AEROGELS

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ABSTRACT

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The formation of monolithic and transparent transition metal containing aerogels has been achieved through cooperative interactions of high molecular weight functionalized carbohydrates and silica precursors, which strongly influence the kinetics of gelation. After initial gelation, subsequent modification of the ligating character of the system, coordination of the group VIII metal ions, and supercritical extraction afford the aerogels. The structures at the nanophase level have been probed by photon and electron transmission and neutron scattering techniques to help elucidate the basis for structural integrity together with the small entity sizes that permit transparency in the visible range. They also help with understanding the chemical reactivities of the metal-containing sites in these very high surface area materials. These results are discussed in connection with new reaction studies.

INTRODUCTION

There is considerable interest in the formation and properties of gels and aerogels based on silica. Some of this arises from the possibility of incorporating metal-containing species in the materials so that they can be used as precursors of catalysts. The catalysts then would be formed as composites containing metal particles [1] or metal oxide [2] or other metal complex compounds. That has lead to a range of studies of transition metal species in silica aerogels [3,4].

In this work, a general synthetic approach has been taken that is designed to provide for both the incorporation of metal ions and the preservation of other advantageous features of aerogels. These advantages can include more than just low density and high porosity. Indeed, some silica-based aerogels are monolithic structures with useful optical, thermal and electronic applications. Formation of transparent, monolithic metal ion containing aerogels potentially provides a way to attain a class of materials with these attributes as well as those imparted by metal ions.

The primary reported methods for incorporation reported to date include adsorption of metals from solution by functionalized aerogels. This is a method for the clean up of metal-ion contaminated sites [5]. It also includes the incorporation of transition metal complexes, such as copper amine complexes [6]. And, it includes the formation of complexes in aerogels through the reactive attachment of a complexing ligand into the sol-gel structure [4].

The approach reported here is to form a silica-and polymer-based aerogel in which the polymer can provide metal ion coordination sites for a range of metal ions. In order to be transparent, the gel must be formed at low enough pH to obtain nanometer scale fundamental particle sizes. The polymer must have the ability to strengthen the gel sufficiently to allow for the formation of an aerogel monolith. The polymer also must have the ability to provide useful metal ion coordinating sites in pH ranges at which the silica structure and particles size distribution are stable.

It is difficult to find materials and approaches to achieve this. The silica related structures are very small when they are formed at relatively high levels of acid, which correspond to pH values of less than 5 in the aqueous solution equivalent acidities. However, at

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these levels of acidity, the coordinating sites of polymers tend not to be in the forms that are favorable for complexation. For example, amine-sites usually have effective pK_a values such that they are overwhelmingly in the $-NH_3^+$ form at pH less than 7, with typical pK_a values of 9 – 10. Acid sites are somewhat more available for ionic association, but their form also is strongly pH dependent. Relatively few polymers are water soluble or soluble in the presence of reacting TEOS and its hydrolysis products. Those that are water soluble tend to have pH dependent shapes and functionalities. Finally, the polymeric materials that one can consider for this approach tend to be extractable from the wet gels when supercritical fluid extraction is employed, so it is necessary to prevent that from happening.

The types of polymers chosen for this study are polysaccharides of the type known as chitosans. These are partially or fully deacylated forms of chitin. At the sites of deacylation, typically 85% of the acyl amine groups of chitin, the functional group is an amine. A representation of a fully deacylated form of chitosan is shown below. Chitosan polymers with

this level of deacylation are soluble in aqueous acetic acid solution, and can form clear sols with gelling silica sources such as tetraethoxysilane (TEOS). Chitosan's hydroxyl groups as well as its other oxygen atoms provide ways for it to be solvated and for it to interact with moieties of the silicon-containing species condensing to form the gel. They and the amine groups can interact both with the silica-containing portion of a gel, and they can interact with metal ions. The amine groups, in particular, act as coordinating ligands when the pH is high enough.

As mentioned above, the typical amine has a pK_a that is well above 7, but it is a special characteristic of chitosan that its pK_a is effectively about 6.5[6]. Despite numerous studies of the compound, it is not clear why that is its effective pK_a . It presumably results from a combination of factors involving the site properties, polyelectrolyte effects, and intermolecular hydrogen bonding effects. Because of this, value, it is able to have a reasonable fraction of its amine sites in the form of NH_2 at pH 6.6 or less. This makes it possible for it to complex transition metal ions at pH values below those at which a silica network is depolymerized[7].

The combination of aqueous solubility, functional groups that could interact with a silica network, and amine groups that could provide general complexation sites for a wide range of transition metal ions made chitosan an interesting polymer with which to explore the possibility of forming transparent monolithic transition metal-containing aerogels[8-10].

EXPERIMENTS

The synthesis of the aerogels described here involves first the formation of a solution of chitosan (Fluka Biochemika, M_r of about 2,000,000, degree of deacylation 84.5%) in aqueous acetic acid. Typically 0.4g chitosan and 0.4mL glacial acetic acid were combined with 40 mL water[8,9]. The solution was mixed with 12.5 mL TEOS (Tetraethoxysilane, Fluka Chemika), an additional 0.9mL glacial acetic acid was added and the mixture was stirred vigorously. After 8 hours, the initially heterogeneous mixture was a clear sol. Some of the sol was placed in a

container to a depth of 1-3 mm, covered and allowed to gel and age for another 8 hours. Then it was treated with dilute ammonium hydroxide in absolute ethanol (ca. 2-3 drops of 29% (w/w) ammonium hydroxide in 50 mL ethanol). This solution was decanted after 24 hours and the gel was treated with absolute ethanol twice over 48 hours to replace the remaining water with ethanol. These gels were dried with supercritical CO₂ using a CCS 3100-1000 supercritical drier. Series of chitosan-silica aerogels were prepared in this manner with chitosan concentrations ranging from 5 to 20 % (w/w).

In the case of the transition metal ion-containing gels, the gels were reacted with a metal salt dissolved in absolute ethanol. For example, a 0.01 M solution of RuCl₃ (Strem Chemicals) was added to the ethanol exchanged gel from the initial procedure. In the case of a 2% (w/w) Ru chitosan silica aerogel, mentioned below, the initial gel contained 10% (w/w on solids) chitosan and 90% (w/w on solids) silica and it was exposed to this 0.01M solution for 48 hours. The metal ion solution was replaced by an absolute ethanol solution. Then the gel was dried in supercritical CO₂. Other metal-containing aerogels of this type have been made with Rh(III), Co(II), Ni(II), Cu(II), Pt(II), and Pd(II) [8-10].

Physical properties were measured as follows. The surface areas were measured by standard multipoint BET methods using N₂ and H₂ on a Quantasorb surface area analyzer. Refractive indices were measured at 632.8 nm with a Metricon Model 2010 Prism Coupler with a He/Ne laser and a 200-P-4 prism. Infrared transmission measurements were made using an IBM/Bruker FV 130 FTIR spectrometer.

Structural studies [9,10] were carried out by high resolution transmission electron microscopy (TEM) in collaboration with David Pickles of Corning, Inc. The image presented here was measured on the edge of a fractured piece of aerogel. Small angle neutron scattering (SANS) studies were carried out at the Argonne National Laboratory (ANL). The SANS of the monolithic aerogels (placed between quartz windows) were measured with a time-of-flight instrument, SAD, at the Intense Pulsed Neutron Source at ANL. SAD uses neutrons from a solid CH₄ moderator at 24 K with a wavelength from 5 to 14 Angstroms (Ang). This instrument provides data in a Q (wave vector) range of 0.005 - 0.35 Ang⁻¹ in a single measurement.

Chemical reaction studies have been carried out to explore the reactions of these metal ion-containing aerogels with small molecules, such as CO(g), H₂(g), and NO(g), which are of interest in catalysis and gas detection[10]. Thin monolithic aerogels were placed in a stainless steel reactor fitted with KBr windows. The temperature of the sample and the composition and pressure of the gases were controlled and measured. The reactions shown here are those of Ru(III) chitosan aerogels with the composition given in the preparation described above. They were treated with according to the procedures designated in the following section and the captions to the figures in which spectral results are shown.

RESULTS AND INTERPRETATION

The monolithic aerogels produced by this method have been made in pieces of about 5 cm x 5 cm x 0.2 cm, although they typically are prepared in a thinner form to facilitate spectroscopic study. They are clear and have the low densities and refractive indices illustrated in Table I. Their colors and, more fully, their visible spectra depend on the properties of the metal ions they contain[8].

Structural studies were carried out to discover two aspects of the structures formed in these materials. The most obvious aspect involves the question of whether the chitosan remains in the aerogel after the various washing and solvent exchange processes and the supercritical drying procedure. A related question has to do with the functioning of such chitosan as a metal ion-coordinating ligand. The second main aspect of the structural studies has to do with the

Table I
Physical Properties of Typical Silica-chitosan-metal ion Aerogels

Sample Name	Density (g/cm ³)	Refractive Index at 632.8nm	BET Surface Area (m ² /g)*	Metal Content (mass %)
Silica-chitosan aerogel (10%(w/w) chitosan)	0.25	1.14	600	-
Co(II) silica- chitosan aerogel*	0.26	1.14	800	0.7%
Rh(III) silica- chitosan aerogel*	0.27	1.17	950	0.5%
Ru(III) silica- chitosan aerogel*	0.27	1.17	800	2.0%
*(all based on initial 90% silica/10% chitosan dry mass ratio compositions)			*observed from 500 to given value on range of measurements	

morphology. Specifically, the questions here concern the sizes of the ultimate nanoscale objects and how they are joined or collected together.

The first aspect can be addressed spectroscopically. The infrared spectra of three chitosan-silica aerogels without metal ions are shown in the *ca.* 1325–2200 cm⁻¹ range in Figure 1. The growth of the amine related band marked on the spectrum shows that the chitosan content in the aerogel grows with its content in the initial sol-gel. The FTIR spectrum of a chitosan-silica aerogel and an analogous aerogel with Ru(III) but otherwise the same composition is shown in Figure 2. Clearly, the band associated with the free amine in the aerogel without metal ions is reduced when the metal ions are present. Moreover, the band assigned to the metal ion-coordinated amine is present in the case of the Ru(III)-containing aerogel. The first issue seems to be resolved with these and analogous FTIR and ultraviolet-visible-near infrared spectral studies [8–10]. The chitosan is present and does participate in the coordination of the Ru(III) ions in this case. The details of the coordination vary with metal ion, since each has a unique set of thermodynamic and kinetic properties.

The second aspect has been addressed by a combination of TEM and SANS studies. They are informed initially by the fact that the aerogels are clear, so there are not ultimate particles larger than about 0.2 microns. The TEM images show that the ultimate particle sizes are much smaller than that [10]. The TEM image for the chitosan-silica with 10% chitosan is shown in Figure 3. As shown there, the fundamental particles are quite small. The scale makes it clear that they are much less than 10 nanometers in breadth. It is clear on close examination that this breadth is on the order of 1 to 2 nm. However, it also seems that there might be a somewhat larger scale order in which the fundamental particles are connected. The images are of high enough resolution only to permit speculation that such connected structures could have a coherence that extends over a few of the fundamental objects. This would correspond to about 3 to 8 nm.

Figure 1. Infrared spectra in the 1325 to 2200 cm^{-1} range of chitosan-silica aerogels with varied chitosan contents. Spectra offset arbitrarily for display.

Figure 2. Infrared spectra in the 1325 to 2200 cm^{-1} range of a chitosan-silica aerogel and no metal ion and one with Ru(III) present, as indicated. Spectra offset arbitrarily for display.

Figure 3. Transmission Electron Micrograph of a chitosan-silica aerogel containing 10% by weight of chitosan; the distance scale is indicated on the micrograph. TEM measured by D. Pickles [8].

The SANS experiments are a powerful complement to the TEM images, since they also probe on the nanometer scale. The SANS scattering data measured on a series of the transparent monolithic chitosan-silica aerogels with varied chitosan content but without metal ions are shown in Figure 4. The aerogels containing transition metal ions also have been studied by SANS [10]. The analysis of SANS data proceeds through a model fitting approach, as has been widely discussed [11-13]. In this work, the data have been fitted with a small particle mass fractal model equation derived from the Teixeira model for mass-fractal aggregates of spheres [11]. The scattering function used here is given by the following equation, where I_{0A} is the

$$I(Q, \xi, D_F) = I_{0A} \frac{\sin[(D_F - 1)\arctan(Q\xi)]}{(D_F - 1)Q\xi(Q^2\xi^2 + 1)^{\frac{D_F - 1}{2}}} + I_{\text{Background}}$$

overall intensity scattered by the aggregate extrapolated to $Q = 0$, D_F is the mass-fractal dimension, ξ is the exponential cutoff for the aggregate, and $I_{\text{Background}}$ is the background intensity. The detailed differences between this and the Teixeira model are discussed elsewhere [10]. Briefly, the model is a valid approximation when the scattering from the form factor for the fundamental sphere is not visible or, alternatively, whenever $\xi \gg R$ (the radius of the spheres in the Teixeira model) and $Q_{\text{max}}R \ll 1$, where Q_{max} is the value of Q at which the power law scattering fades into the background scattering.

The analysis in terms of this model in the case of the chitosan-silica aerogels without metal ions results in fractal dimensions of 2.60 for 5% chitosan to 2.52 for the 10% chitosan aerogel. This compares to the dimensionality of 2.85 for the aerogel prepared without chitosan but with all other synthetic conditions held constant. The 20% and additional weight percentage

Figure 4. Small Angle Neutron Scattering data for chitosan-silica aerogels with 0, 5, 10 and 20% by weight of chitosan; as indicated by the symbols, the curves are in order of concentration from bottom to top.

chitosan aerogels remain under study. The fractal dimensionality decreases on going from the silica to the silica-chitosan aerogels, however the exponential cutoff length increases quite significantly from 3.25 nm to 5.74 nm in the 10% chitosan aerogel. The metal ion-containing materials based on 10% chitosan content initial gels, including Ru-, Rh- and Co- containing aerogels, typically have fractal dimensions in the 2.45 to 2.60 range. The corresponding exponential cutoff lengths are in the 5.8 to 7.9 nm range. These lengths are exponential cutoff lengths and are not directly object dimensions, but it is interesting to note that they are on the order of 3 to 6 times the diameter of the smallest fundamental objects seen by TEM.

Chemical reaction studies have been carried out to ascertain the extent to which these aerogels in the form of group VIII metal ions would be suitable for catalytic and gas absorption applications. The primary attention has been devoted to those containing either Rh(III) or Ru(III) ions coordinated to the chitosan and, to some extent, to the available sites on silica-rich moieties of the aerogels[9]. They display an extensive chemistry. Not only do the metal ions and added gases react, but the water associated with the aerogel can play an important role. This is shown by the following reactions of Ru(III) aerogels, which have extensive precedent in the reactions of other supported Ru(III) systems [14-17].

The availability of large thin monolithic aerogels makes it possible to measure the infrared spectra of the aerogels and their reaction products directly by transmission spectroscopy. Because of the compositions, the region of about 1500 to about 2600 cm^{-1} has low enough absorbance to act as a window to observe reactions involving CO(g), H₂(g), and NO(g) as well as some of the effects of water and oxygen.

When a hydrated Ru(III) aerogel is formed in the reactor by exposing the aerogel to water vapor at 20°C for 10 minutes, it reacts with CO to form metal carbonyls with bands at 2081 and 2018 cm^{-1} , as well as a band at 1972 cm^{-1} . This is shown in curves A and B of Figure 5. On the

Figure 5. Infrared spectra of Ru(III) chitosan-silica aerogel with 2% Ru(III) and its reaction products where:

- A. initial sample, dehydrated at 95°C for 7 hr *in vacuo*
- B. A exposed to 0.4 atm. CO; 11 hr at 20°C
- C. B exposed to 1.0 atm. H₂; 24 hr at 95°C
- D. C exposed to 0.1 atm CO; 4 hr at 95°C

Figure 6. Infrared spectra of Ru(III) chitosan-silica aerogel with 2% Ru(III) and its reaction products where:

- A. initial sample, hydrated at 20°C for 10 min. in saturated H₂O vapor.
- B. A exposed to 0.1 atm. CO; 12 hr at 20°C
- C. B dehydrated for 2 hr at 95°C
- D. C exposed to 0.1 atm CO; 3 hr at 95°C

other hand, the reaction of a dehydrated Ru(III) aerogel with CO under essentially the same conditions but with a much higher CO pressure does not yield the 1972 cm^{-1} band. Thus, curves A and B of Figure 6 do not show such a band. The fact that it is formed when water is present and not when it is absent is quite interesting.

One reasonable hypothesis to explore is that water reacts with CO at these metal sites to form hydrogen through a form of the water gas shift reaction. The hydrogen would then reduce the metal and the reduced metal would form the new carbonyl associated with the 1972 cm^{-1} vibration. The CO-reacted dehydrated Ru(III) aerogel sample was next reacted with hydrogen for 24 hours at 95°C in order to achieve the reduction without water. However, no significant change occurred in the carbonyl region of the spectrum (see Figure 6 C). Thus, the sample was again reacted with CO, and the spectrum shown in Figure 6 D was observed. It does not provide strong evidence for a 1972 cm^{-1} band. Meanwhile, the species giving rise to the 1972 cm^{-1} band is quite stable, as shown by its presence throughout heating and CO reaction processes in Figure 5 C and D.

These two sets of reactions show that the Ru ions are reactive. There appear to be at least two types of metal carbonyls formed. The 2082 and 2018 cm^{-1} bands appear together at constant relative intensity. They are assigned to the same species, which probably is a dicarbonyl. The 1972 cm^{-1} band is assigned to a carbonyl vibration on a reduced Ru. The spectra both show bands near 2140 cm^{-1} due to adsorbed CO.

These assignments are consistent with known carbonyl chemistry and extensive catalysis literature [14-17]. However, they do not answer the question posed by these results: why does hydrogen from the water gas shift reaction reduce Ru(III) while hydrogen, added in the reaction sequence followed here does not? This appears to be quite unusual, and it may be due to another feature of the hydrated aerogel structure. That structure has a mechanism for forming and possibly transporting hydrated protons, a reduction reaction product. This could favor the reduction reaction in the hydrated aerogel case. That hypothesis and others related to water in the coordination sphere of the Ru(III) ion are under study.

It is clear from a number of the studies on these aerogels that the Ru can assume a range of environments and oxidation states. The spectra of Ru(III) aerogels reacted with NO and CO, in sequence, show the significance of such changes. The reaction of a dehydrated Ru(III) aerogel with NO leads to the product whose spectrum is given as Figure 7 B, with a metal nitrosyl vibration at 1894 cm^{-1} . The subsequent addition of CO leads to metal carbonyl bands at frequencies near their positions in Figure 6. Thus, they are at 2026 , 2085 and 2140 cm^{-1} vs. 2018 , 2080 and 2140 cm^{-1} , respectively. The subsequent addition of NO leads to a significant change, however, since the bands shift to 2036 , 2092 and 2154 cm^{-1} . These shifts together with

Figure 7. Infrared spectra of Ru(III) chitosan-silica aerogel with 2% Ru(III) and its reaction products where:

- A. initial sample, dehydrated at 95°C for 6 hr *in vacuo*
- B. A exposed to 0.1 atm NO; 0.5 hr at 20°C
- C. B exposed to 0.2 atm CO; 18 hr at 95°C
- D. C exposed to 0.05 atm NO; 3.5 hr at 95°C

the symmetrical shapes of the bands indicates that the NO addition had the effect of increasing the effective oxidation state of the Ru(III) in at least the case of the dicarbonyl, to which the 2036 and 2092 cm^{-1} bands are assigned. The interpretation is more tentative in the case of the 2154 cm^{-1} band. It may not be due to physically adsorbed CO, as was suggested for the *ca.* 2140 cm^{-1} band in Figures 5 and 6. In Figure 7, the 2154 cm^{-1} band is stronger relatively, and it is at a quite high frequency relative to the vibration of free CO. The tentative assignment of this band is to a Ru(III) monocarbonyl whose bonding mode is primarily through dative interaction of Ru(III) with the sigma antibonding orbital of CO. This type of interaction can serve to strengthen the CO bond relative to that in CO itself.

CONCLUSIONS

The incorporation of chitosan, a functional polymer that is able to form a clear sol with hydrolyzing TEOS and to interact with both the silica and added metal ions, has been shown to lead to the formation of monolithic, transparent silica-based aerogels of low density and refractive index, and high surface area. They have ultimate particle sizes of less than about 2 nm, as judged from TEM observations. The study of their structure by SANS indicates that they are more generally described by a fractal model with dimensionality between 2.45 and 2.60 and exponential cutoff lengths of 5 to 8 nm. These may be compared to the values of 2.85 and 3.25 nm for silica aerogels made under the same conditions. The metal ion containing aerogels exhibit an extensive reaction chemistry, as illustrated by the reactions of Ru(III) aerogels with CO, H₂, NO and H₂O.

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FIG 3 IMAGE