Formation and Structure of a Tin−Iron Oxide Solid-State System with Potential Applications in Carbon Monoxide Sensing through the Use of Cyanogel Chemistry

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The reaction of aqueous solutions of $SnCl_4{\cdot}5H_2O$ and $K_4Fe(CN)_6$ in a 2/1 Sn/Fe atomic ratio results in a hydrogelled polymeric material, characterized by bridging cyanides between the central metals of the adducts. Materials of this type have previously been noted upon reaction of $PdCl_4^{2-}$ with cyanometalates in aqueous solution and have been referred to as cyanogels. Dehydration of Sn/Fe cyanogels results in xerogels that maintain the initial polymeric structure of the hydrogel. Thermal processing of such gels under an air atmosphere at 900 °C produces a solid homogeneous mixture of microcrystalline SnO_2 and Fe_2O_3.

Introduction

Much of solid-state, gas sensor technology has focused on the conductivity of SnO_2.[1] SnO_2 is a wide-band-gap ($E_g \sim 3.6$ eV) n-type semiconductor, which is therefore expected to act as an insulator at ambient temperature.[2] The use of tin(IV) oxide in gas sensors represents a specific example of the catalytic oxidation properties of the oxide in which bulk electronic changes are of paramount importance. Although it is now only one of many materials that have been utilized in the fabrication of gas sensors, historically it was one of the first employed[1] and has remained at the forefront of the technology for over two decades. One improvement to the initial SnO_2 sensor system has been the introduction of Fe^{III} sites. Such sites are catalytic in nature allowing for reduced sensing temperatures to be employed.[2]

We report here a novel procedure for the preparation of a tin−iron oxide solid-state material by sol−gel processing of a tin−iron-based cyanogel. Previous examples of cyanogel systems are hydrogels formed by the reaction of aqueous solutions of K_2PdCl_4 and $K_xM(CN)_n$ where $n = 4-8$ and M is a transition metal**.** We refer to such materials as cyanogels because the hydrogel product is characterized by bridging cyanides between the two metal centers forming a star-polymer system.[3] Prior to the work reported here, it appeared that $[PdCl_4]^{2-}$ was the only workable non-cyanide transition-metal reagent.

Hydrogel systems containing the tin−iron cyanide moiety have not previously been reported in the open literature. However, there exists very limited literature considering the thermal chemistry of the tin cyanoferrate compounds. In one set of papers the authors described the preparation of the nongelled, solid, $Sn[Fe(CN)_6]$ and its use as an inorganic ion exchanger.[4−8] Additionally, the thermal decomposition of unsupported and supported solid-state $Sn_3[Fe(CN)_6]_4$ in air was studied by IR and Mössbauer spectroscopies.[9] The first stage of decomposition was reported to be evolution of cyanogen, $(CN)_2$, resulting in the reduction of Fe(III) to Fe(II) and formation of Prussian Blue. Further heating of the material above 400 °C resulted in the formation of two Fe(III) oxides, one of them being Fe_2O_3. In a separate study the thermal decomposition of polycrystalline $Sn[Fe(CN)_6]{\cdot}2H_2O$ in air was evaluated.[10] At 150 °C Prussian Blue was reportedly formed and subsequent

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Table 1. Products of Reactions between Tin Chlorides and Iron Cyanides

	$SnCl_4{\cdot}5H_2O$	$SnCl_2{\cdot}2H_2O$
$K_3Fe(CN)_6$	white precipitate, colored deeply blue after 2 weeks	white precipitate
$K_4Fe(CN)_6$	white gelatinous material, used for further processing	white precipitate, deep blue after 2 weeks
$K_3Co(CN)_6$	yellowish solution, no precipitation after 2 weeks	yellowish gelatinous precipitate

heating at 300 °C led to the formation of Fe_2O_3 and SnO_2.

A discrete molecular system has been described in the literature in which Sn/Fe complexes characterized by bridging cyanides are formed from potassium ferrocyanide and organotin compounds such as SnR_3Cl.[11] However, due to the limited number of bridging cyanides formed in these systems, a gel is not formed and the thermal chemistry has been found to be rather different from what we present here.

The present work reports the preparation and structural properties of the tin−iron mixed oxide material obtained by sol−gel processing. To the best of our knowledge, this work represents the first effort to synthesize an iron−tin oxide material using a sol−gel approach.

Experimental Section

Starting materials $SnCl_4{\cdot}5H_2O$ and $SnCl_2{\cdot}2H_2O$ were obtained from Fisher Scientific Co., and $K_3Co(CN)_6$, $K_3Fe(CN)_6$, and $K_4Fe(CN)_6$ from Aldrich. All compounds were reagent grade and used as received. The gels that were studied in more detail were prepared by mixing aqueous solutions of 0.3 M $K_4Fe(CN)_6$ and 0.3 M $SnCl_4{\cdot}5H_2O$ at room temperature. Deionized water was utilized for all solutions. The gelation took place instantly after mixing the solutions together. Xerogels were prepared by spreading the gels on filter paper and then oven drying at 95 °C to remove water. Xerogels were sintered either in a quartz tube inserted into a furnace or as a sample in a thermogravimetric (TGA) balance. In both cases, the atmosphere above the sample was purged with a constant flow of either air or oxygen using a flow rate of 60 mL/min. **The highly hazardous evolved gases [$(CN)_2$ and HCN] were trapped by a series of two aqueous solutions. The first bubbler contained bleach and the terminal bubbler contained a NaOH solution. Sintering of bulk samples was carried out in a fume hood.**

UV−visible spectra were recorded using a HP 8452A diode array spectrophotometer. FTIR spectra were obtained in the 4000−400 cm^{-1} range on a Nicolet 730 FTIR spectrometer. Samples were prepared between CaF_2 plates or as KBr disks. Thermal analyses were recorded on a Perkin-Elmer TGA-7. Calorimetric data was obtained using a Perkin-Elmer DSC-7. About 10 mg of the xerogel was used for each analysis, performed at a heating rate of 6 °C/min. X-ray powder diffraction (XRPD) analyses were obtained on Scintag PAD V ($\theta-2\theta$) X-ray powder diffractometer using a Cu Kα X-ray source and a solid-state germanium−lithium detector. Samples were scanned from the quartz zero background at a rate of 1°/min.

The chemical composition of the mixed oxides was studied by electron probe microanalysis (EPMA) using a CAMECA SX-50 instrument. High spectral resolution X-ray measurements were made using crystal monochromators and gas flow X-ray detectors. Analyses were performed using an accelerating voltage of 15 kV and a regulated beam current of 20 nA. Both secondary and backscattered electron images were used to locate areas suitable for analysis. The spatial resolution for a point analysis was approximately 1 μm^3 for the above instrumental conditions.

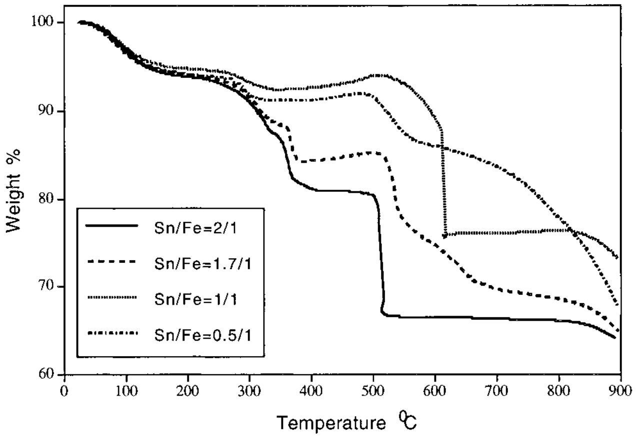

Figure 1. TG curves for the Sn/Fe xerogel at four different ratios. The thermal endpoint for cyanide loss is lowest for the Sn/Fe = 2/1 ratio, indicating that both components react in that ratio.

To test the properties of the tin−iron mixed oxide material as a gas sensor, electrical conductance measurements were performed in a quartz tube inserted in a tube furnace. The electrical contact was obtained using copper tape on a pressed pellet sample. A two-contact configuration was employed. The pellets were maintained at a working temperature of 400 °C for about 30 min before measuring the increase of the electrical current in response to a defined CO/argon mixture.

Results and Discussion

Mixing 60 mM aqueous solutions of $K_3Co(CN)_6$, $K_3Fe(CN)_6$, or $K_4Fe(CN)_6$ with either $SnCl_4{\cdot}5H_2O$ or $SnCl_2{\cdot}2H_2O$ resulted in very different products as depicted in Table 1. The products obtained after reacting 0.3 M $SnCl_4{\cdot}5H_2O$ with 0.3 M $K_4Fe(CN)_6$ in different volume ratios, resulted in white homogeneous gels. The gel prepared with a Sn(IV)/Fe(II) = 2/1 ratio proved to be the most stable over a period of several days (did not change color or expel water), so this system was selected for the further analysis.

$SnCl_4$ is soluble in water,[2] but subject to hydrolysis, and in the absence of strong complexing anions, aqueous solutions of Sn(IV) tend to hydrolyze to give precipitates of hydrous tin(IV) oxide.[2] Thus, as soon as $SnCl_4{\cdot}5H_2O$ was completely dissolved in water, forming a colorless solution, and before the precipitation of tin(IV) oxide could occur, it was mixed with ferrocyanide to form the gels noted above.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) Data. TGA was performed on xerogels of four samples with different Sn/Fe ratios as shown in Figure 1. The xerogels contain about 7% residual water which is lost at 100 °C. The decomposition of the cyanogels starts at around 250 °C. Weight loss in the 250−400 and 490−510 °C ranges is associated with the loss of the cyanide ligands as cyanogen. The oxidation of cyanogen by O_2 is an extremely exothermic reaction,[12] as seen in the DSC curve (Figure 2), of the Sn/Fe = 2/1 xerogel. In the TGA curve,

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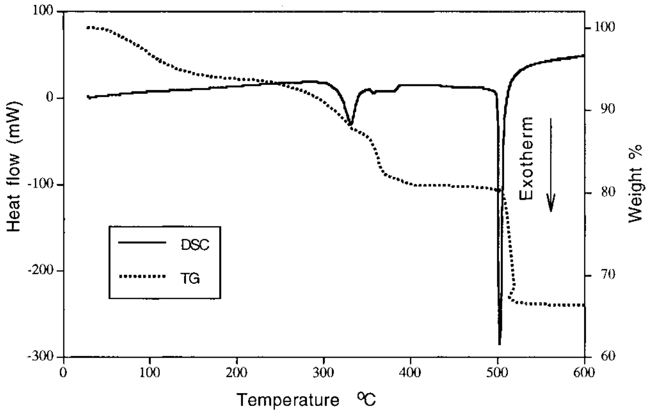

Figure 2. DSC and TG curves of Sn/Fe = 2/1 xerogel. Mass loss in the 250−400 °C is associated with the exothermic reaction of evolved cyanogen with O_2.

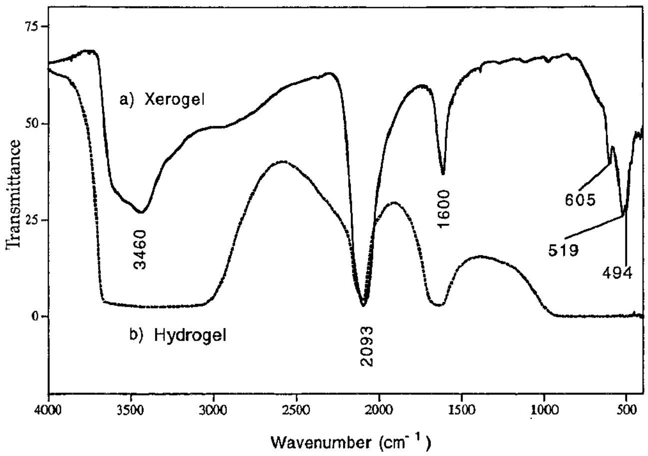

Figure 3. IR spectra of (a) Sn/Fe = 2/1 xerogel and (b) Sn/Fe = 2/1 gel before drying. The two peaks near 3500 and 1600 cm^{-1} are due to water. The cyanide stretching vibration, ν(CN), has a frequency of 2093 cm^{-1}. In the low-frequency region, overlapping ν(FeC) and ν(SnO) stretching vibrations are assigned to the 519 and 494 cm^{-1} peaks. The broad 605 cm^{-1} peak is assigned to the δ(Fe−CN−Sn) bending modes.

shown in the same figure, the advancement of the sample temperature above the temperature of the TGA furnace can be seen around 505 °C, which is a gain indicative of an extremely exothermic reaction. The thermal end point for cyanide loss is the lowest for the xerogel with the Sn/Fe = 2/1 ratio, which suggests this is the stoichiometric ratio of the cyanogel product. All other xerogels synthesized with a Sn/Fe ratio lower than 2/1 contain an excess of non-tin-bonded ferrocyanide, which starts to decompose slowly only at temperatures above ~500−550 °C, as seen in Figure 1. No change of mass in the 650−700 °C region was detected, but a mass loss is seen again in 800−900 °C, which is associated with KCl sublimation.[13]

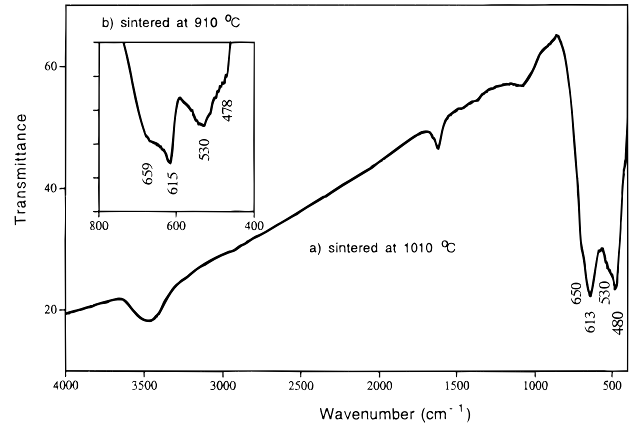

Figure 4. IR spectra of the Sn/Fe = 2/1 sample sintered at (a) 1010 °C for 17 h and (b) at 910 °C for 96 h in air atmosphere. Low-frequency vibrations are attributed to Sn−O and Fe−O stretching vibrations, indicating the formation of a mixed oxide.

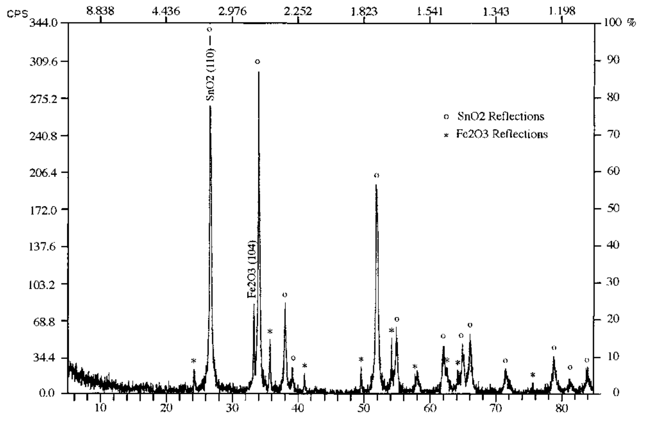

Figure 5. XRPD of the Sn/Fe = 2/1 xerogel after sintering in an air atmosphere at 910 °C for 3 h indicating the presence of Fe_2O_3 and SnO_2 in the sintered sample.

Infrared Spectroscopy of Iron−Tin Cyanogels and Thermal Products. The IR spectrum of $K_4Fe(CN)_6$(aq) has one sharp stretching vibration ν(CN) at 2037 cm^{-1}, and two in the low-frequency region, a stretching vibration, ν(FeC), at 565 cm^{-1} and a bending vibration, δ(FeCN), at 417 cm^{-1}, as assigned previously.[14] The IR spectrum of the Sn/Fe = 2/1 gel shows a shift of the cyanide stretching vibration, ν(CN), to a higher frequency, 2093 cm^{-1} (see Figure 3b) which corresponds to the formation of bridging cyanides (Fe−CN−Sn), by analogy to similarly bridged species.[3,14,15] The total loss of the original vibration indicates the quantitative conversion of terminal cyanides to bridging cyanides during formation of the hydrogel. Infrared spectroscopy of the hydrogel is hindered by the fact that the cyanide stretching vibrations in the 2000−2200 cm^{-1} region and below 700 cm^{-1} are overlapped by the water vibrations. However, this problem can be circumvented by carrying out IR analysis on the xerogels, which maintain the original structure of the gel as shown in the Figure 3a.

The two large peaks in the spectrum of the xerogel (Figure 3a) near 3500 and 1600 cm^{-1} are due to residual water in the xerogel. In the low-wavenumber region, there is a major peak at 519 cm^{-1} with a shoulder at 494 cm^{-1} which we assign to the overlapping ν(FeC) and ν(SnO) stretching vibrations, and a broad peak at 605

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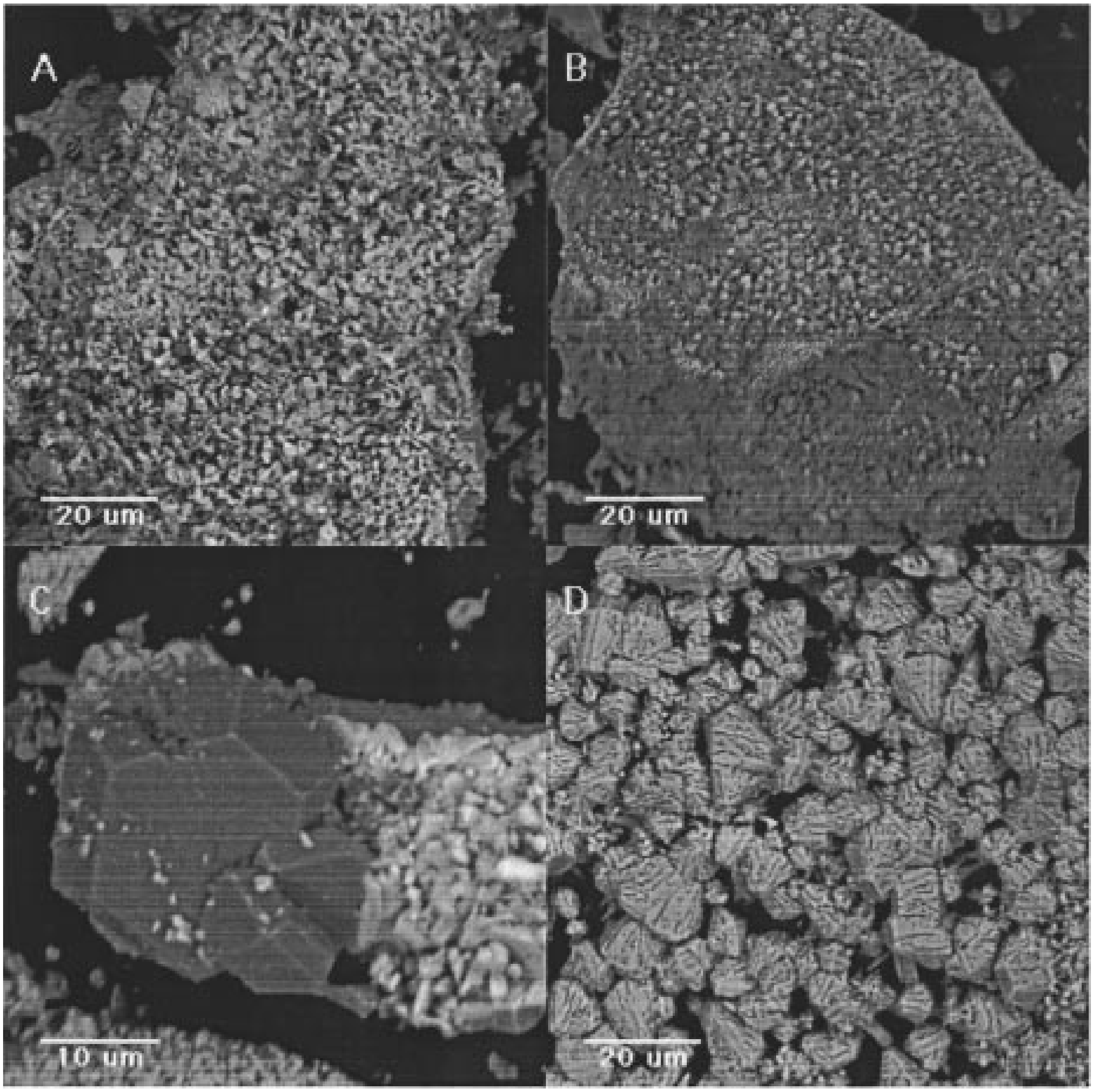

Figure 6. Backscattered electron-generated images of thermalized products formed from (a) Sn/Fe = 1/2 xerogel (nonhomogeneous mixture of Fe_2O_3 and SnO_2), (b) Sn/Fe = 2/1 xerogel (homogeneous mixture of Fe_2O_3 and SnO_2), (c) Sn/Fe = 3/1 xerogel (Fe_2O_3 crystal on SnO_2), and (d) Sn/Fe = 4/1 xerogel (SnO_2 crystals with needles of Fe_2O_3). In all cases the xerogel was sintered in an air atmosphere at 910 °C for 3 h.

cm^{-1} assigned to the δ(Fe−CN−Sn) bending mode.[16−18] In the far-IR region, there is a peak at 320 cm^{-1} which is in the region that ν(SnCl) stretching vibrations characteristically occur.[14] Since both ν(SnO) and ν(SnCl) are found in the xerogel product, it can be concluded that the $SnCl_4 \cdot 5H_2O$ reactant is partially hydrolyzed during the synthesis of the cyanogel. An additional shoulder to the 2093 cm^{-1} peak was observed at 2135 cm^{-1} in the IR spectra of the xerogel having a ratio of Sn/Fe = 1/1 and at 2041, 2114, and 2135 cm^{-1} in the Sn/Fe = 1/2 gels, corresponding to an excess of ferricyanide and/or ferrocyanide, trapped in the gel. Thus, the IR spectra supports the hypothesis that the stoichiometry of the polymeric cyanogel is 2:1 Sn:Fe.

A Sn/Fe = 2/1 xerogel, thermolyzed at 900 °C under an air atmosphere for 3 h, shows new vibrations at 659, 615, 530, and 478 cm^{-1} (see insert to Figure 4), attributed to Sn−O and Fe−O stretching vibrations,[2,19,20] and indicating the formation of a mixed oxide or mixtures of oxides. Over the same reaction period all C−N stretching vibrations are lost, indicating the decomposition of the cyanides. The IR spectrum of solid

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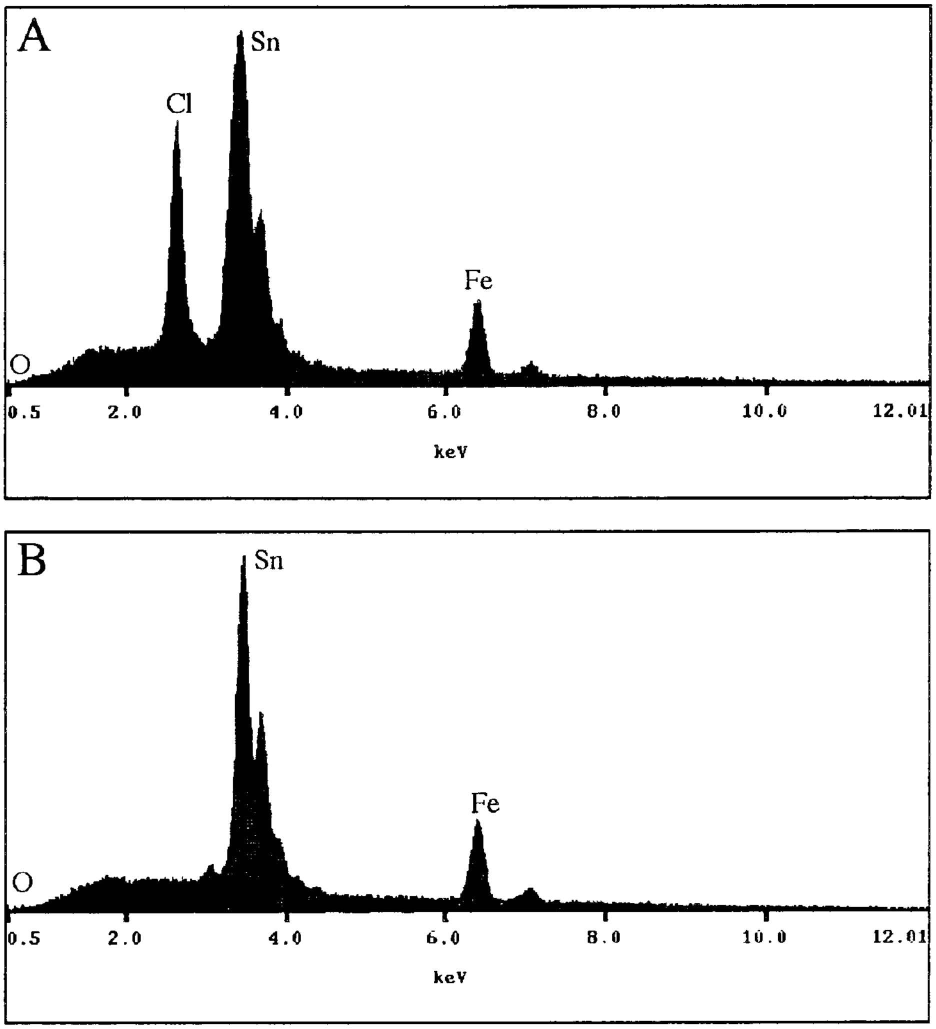

Figure 7. EDX data of Sn/Fe = 2/1 xerogel obtained after heating to (a) 600 °C indicating the presence of of Fe, Sn, O, and Cl, and (b) 910 °C for 3 h indicating the presence of Fe, Sn, and O.

SnO_2, which has nearly regular octahedral symmetry, shows[21] two broad bands at ~610 and 660 cm^{-1}. Hematite in the polymorphic form of α-Fe_2O_3 in turn shows[21] broad vibrations at ~480 and 530–580 cm^{-1}. The oxide material obtained by thermolyzing the same Sn/Fe = 2/1 xerogel at 1010 °C for 3 days shows an IR spectrum with peaks at 650, 615, 530, and 480 cm^{-1} (see Figure 4) consistent with a mixture of these two materials.

XRPD Analysis. The X-ray powder diffraction pattern of the Sn/Fe = 2/1 sample sintered at 910 °C for 3 h in an air atmosphere is shown in Figure 5. The pattern shown corresponds to SnO_2 having the structure cassiterite and α-Fe_2O_3, hematite.[22] When a portion of this sample was treated with hot concentrated phosphoric acid for 5 days, the rust color of the sample was lost, and a subsequent XRPD analysis indicated a loss of Fe_2O_3. Thus, the solid-state product is not a single compound but rather a mixture of tin oxide and iron oxide. There is no evidence in the XRPD analysis of the presence of any other iron, tin, or iron–tin oxide compounds in the sintered material.

Scanning Electron Microscopy and Electron Probe Microanalysis. Four different Sn/Fe ratio xerogels were sintered at 910 °C for 3 h under air, and the final products were examined by SEM. Backscattered electron images of these four samples are given in Figure 6. Only the 2/1 Sn/Fe product (Figure 6b) exhibited a highly homogeneous product. The 4/1 Sn/Fe product (Figure 6c) can be described as crystals of SnO_2 with needles of Fe_2O_3 interspersed. The 3/1 Sn/Fe product (Figure 6d) shows hexagonal crystals of Fe_2O_3 on SnO_2. The 2/1 Sn/Fe and the 1/2 Sn/Fe products (Figure 6a,b) are both a mixture of Fe_2O_3 and SnO_2, determined by XRPD of the samples. But the extremely homogeneous appearance of the 2/1 Sn/Fe ratio appears to be an unique dispersion of microcrystalline Fe_2O_3 in microcrystalline SnO_2. Although beyond the limit of resolution of the SEM, crystallite size is determined to be about 0.1 μm on average, based on the XRPD half-peak width of the SnO_2 (110) reflection and the Fe_2O_3 (104) reflection.[23] These peaks are labeled in Figure 5. The smaller crystallites of the 2/1 sintered xerogel are another indication that this ratio is the stoichiometric ratio for gelation, which allows for the full benefits of sol–gel processing.

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The changes in the material morphology when the Sn/Fe ratio is changed can be understood in terms of the biphasic structure of the hydrogel. In the stoichiometric gel, the starting materials are intimately combined within the cyanogel polymer. Thermolysis of the polymer produces a microcrystalline product due to the amorphous nature of this material (it is not observed to scatter X-rays) and the limited availability of metal centers as established by the stoichiometry of the polymer and coordination environment. When the Sn/Fe ratio is nonstoichiometric, the excess material resides in the aqueous phase within the pores of the cyanogel. When the cyanogels are dried to form xerogels, the nonpolymeric material dissolved in the aqueous phase crystallizes. These large crystals of excess material form large oxide crystals when the xerogel is sintered. XRPD indicates that the average SnO_2 crystallite size is larger when the Sn:Fe ratio increases from 2:1 to 4:1 (an excess of tin). When the Sn:Fe ratio is changed from 2:1 to 1:1 (an excess of iron), the average Fe_2O_3 crystallite size becomes larger.

To obtain compositional data, an EDX analysis was carried out for two samples, one prepared at 600 °C and one generated at 910 °C (Figure 7). Both samples were prepared from a Sn/Fe = 2/1 xerogel. The presence of chloride is observed only in the low-temperature sample, while both samples show the presence of Sn/Fe in a 2/1 ratio. This finding is consistent with the TGA data, which shows the sublimation of KCl above ∼800 °C. Higher resolution elemental analysis including oxygen analysis was obtained from EPMA (wavelength dispersive) measurements. From these measurements a ratio of Sn/Fe/O = 4/2/11 was found. A variety of scans over a wide sample area showed a constant concentration of Fe, Sn, and O throughout the material. On the basis of these data, the product is identified as a highly homogeneous mixture of SnO_2 and α-Fe_2O_3 having a tin oxide to iron oxide ratio of 4:1.

CO Sensing. Preliminary work in our laboratory indicates that when pressed into a pellet, the oxide material shows a good response toward CO. The background conductance of the material, measured in pure oxygen at 400 °C, was 1.7×10^{-6} S which is a typical value for SnO_2 film conductance.[4] The conductance of the material in an atmosphere of 500 ppm CO in oxygen measured at 400 °C was found to be 6.5×10^{-6} S, yielding a sensitivity factor of 3.9 (gas sensitivity is defined as the ratio of sample conductivity in the presence of CO to the baseline conductivity), higher than the sensitivity reported for iron "doped" SnO_2 materials prepared by thermal oxidation (measured sensitivity is 3.2).[6]

The mechanism of CO sensing has been reported to involve the adsorption of CO onto adjacent surface adsorbed $O^{\bullet -}$ species on the SnO_2 surface.[24] This process yields a surface carbonate species, and the subsequent desorption of CO_2 as a product provides a mechanism by which electrons are returned to the conduction band of the oxide, from which an increase in conductance would be expected. The higher sensitivity of the SnO_2/Fe_2O_3 material reported here may be due to the large surface area versus volume ratio and/or higher porosity of the material. The larger surface area provided by the SnO_2/Fe_2O_3 material would allow for more surface adsorbed $O^{\bullet -}$ species to be available for CO adsorption and the subsequent desorption of CO_2 which, in turn, allows for an increase in the number of electrons returning to the conduction band of the tin oxide, increasing the sensitivity of the SnO_2/Fe_2O_3 material. The exact source of the improved sensitivity is presently under study.

Conclusions

Aqueous solutions of $SnCl_4{\cdot}5H_2O$ and $K_4Fe(CN)_6$ react when mixed to form a hydrogel characterized by bridging cyanide ligands between the tin and iron metal centers. IR analysis of the Sn/Fe = 2/1 xerogel indicates the presence of ν(SnCl), ν(SnO), and ν(CN) stretches. Tin(IV) halides act as acceptors and expand to six-coordinate systems to form complexes with donor ligands. Since many diligand complexes of tin(IV) halides with nitrogen donor molecules are known (such as $SnCl_4(NH_3)_2$),[2] we postulate that in the reaction between $SnCl_4{\cdot}5H_2O$ and $K_4Fe(CN)_6$, the four-coordinate $SnCl_4{\cdot}5H_2O$ expands to a six-coordinate complex to form the bridging cyanides, and that the chloride ligands are partially hydrolyzed.

When the Sn(IV)/Fe(II) = 2/1 cyanogel is thermolyzed and sintered at 910 °C for 3 h, XRPD indicates that the product is composed of submicron particles of SnO_2 and Fe_2O_3 with no shoulders or other lines indicating the presence of a SnO_2/Fe_2O_3 solution or other oxides. A product composed of a new iron tin oxide compound would display lines other than that of SnO_2 and Fe_2O_3 in the XRPD pattern due to changes in the crystal lattice structure. This is not observed. EDX and SEM analysis of the product indicate the formation of a very homogeneous material containing a 4:1 ratio of SnO_2 and Fe_2O_3 based on EMPA data. Thus, we conclude that the thermolyzed and sintered product of the Sn(IV)/Fe(II) = 2/1 cyanogel is an exceptionally homogeneous mixture of SnO_2 and Fe_2O_3. Our preliminary results indicate that this material may be employed for the preparation of an improved CO gas sensor.

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