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Formation of a Nanocomposite Containing Particles of Co_3C from a Single-Source Precursor Bound to a Silica Xerogel Host Matrix

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Addition of the alkylidynetricobalt nonacarbonyl complex $(HO)_3SiCo_3C(CO)_9$ to a conventional sol−gel recipe for silica xerogel formation leads to apparent covalent incorporation of this cluster into the skeletal backbone of the xerogel matrix through the heterocondensation of Si−OH groups. Subsequent thermolysis of this purple, molecularly doped xerogel in a hydrogen atmosphere at 500 °C affords a black xerogel nanocomposite containing particles of diameter 10−46 nm. TEM, EDS, XRD, and electron diffraction data indicate that the nanostructured material is predominantly Co_3C with some Co_3O_4 also being present. Formation of Co_3C as the sole cobalt carbide substance detected demonstrates synthetic control of nanoparticle composition through the proper choice of core composition of a molecular precursor.

Introduction

Nanocomposite materials consisting of very small particles (typically nanoscale particles having diameters less than 100 nm) of a guest substance dispersed throughout a host matrix are of intense current interest for potential applications in chemical catalysis or as magnetic, electronic, or photonic materials.[1] Schubert and co-workers have reported that in situ coordination of metal ions to bifunctional ligands containing distal silicate ester groups gives covalent incorporation of metal complexes as dopant species into silica xerogel matrices during conventional sol−gel syntheses. Subsequent calcination and reduction of these silica xerogels doped with metal-ion complexes affords nanocomposites containing metal nanoclusters.[2] We have described an extension of this procedure in which discrete molecular precursors containing similar bifunctional ligands are prepared and used as dopant additives in sol−gel recipes to give silica xerogels containing covalently attached metal coordination complexes, organometallic clusters, or organometallic compounds of main-group elements. Subsequent thermal treatments under reducing or oxidizing then reducing conditions gives nanocomposites containing nanoclusters of metals or semiconductor substances.[3]

We now report that the (trihydroxysilyl)methylidynetricobalt nonacarbonyl cluster complex ($(HO)_3SiCo_3C(CO)_9$, **1**) undergoes heterocondensation with hydrolysis products of tetramethylorthosilicate (TMOS) under conventional sol−gel conditions to give apparent covalent incorportion of this cluster compound as a dopant species into the resulting silica xerogel matrix. Subsequent thermal treatment of this molecularly doped xerogel under a hydrogen atmosphere affords nanoclusters of the known cobalt carbide substance, Co_3C, which has precisely the same atomic composition as the core structure of the molecular precursor. Although several cobalt carbide phases are known, only Co_3C nanoparticles are detected. This result suggests that the elemental composition of a nanoparticle can be controlled synthetically by the appropriate choice of single-source molecular precursor. Of relevance to this report, Fox and co-workers have reported that Co_3C is a preferred metal−carbide catalyst (either with or without support on an inert material) for the reforming of methanol.[4]

Experimental Section

Reagents and Methods. The cobalt cluster complex $(HO)_3SiCo_3C(CO)_9$ (**1**) was prepared using a published procedure.[5] Silica xerogels were formed at 25 °C using standard sol−gel recipes with minor modification of the procedure reported by Sakka.[6] Tetramethylorthosilicate (TMOS) was purchased from Aldrich Chemical Co. All operations were performed at room temperature unless otherwise specified.

Preparation of a Typical Silica Xerogel Doped with $(HO)_3SiCo_3C(CO)_9$ (1). A homogeneous reaction solution was prepared by mixing 0.50 mL (3.41 mmol) of TMOS, 0.26 mL

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of dimethylformamide (DMF), 0.60 mL (33.3 mmol) of water, 292 mg (0.56 mmol) of **1** as a deep purple solid, and 5 mL of methanol. To ensure a homogeneous reaction solution, complex **1** was placed on a piece of filter paper as a dry powder and was then dissolved through the filter paper into the reaction solution by the addition of the required amount of methanol. To the resulting homogeneous deep purple solution was added 0.03 mL of 0.74 M aqueous ammonia to initiate a sol–gel conversion. A rigid gel formed within 42 min. After 24 h, the resulting monolithic pieces of purple gel were washed with methanol until the washings lacked any purple color. The washed gel was dried in a vacuum oven to give 455 mg (98% ceramic yield) of apparently dry, deep-purple xerogel. Anal. Found: C, 4.81; H, 0.86; Si, 24.07; Co, 13.51. An FT-IR spectrum revealed C–O stretching bands of the carbonyl ligands centered at 2065 cm^{-1}.

Preparation of a Typical Co_3C Nanocomposite. A 95 mg sample of purple silica xerogel doped with complex **1** (prepared as described above) was ground to a fine powder and was placed into an alumina boat that was then inserted into a tube furnace. This system was flushed with nitrogen for 5 min and then with hydrogen for 10 min. Under a continuous purge of hydrogen gas, the temperature of the system was raised to 500 °C (as measured by an internal thermocouple positioned over the sample) and was held at that temperature for 2 h. The sample was then cooled to room temperature, and 66 mg (30.5% weight loss) of a black xerogel powder was isolated. Anal. Found: C, < 0.5; H, 1.21; Si, 30.00; Co, 13.40. An FT-IR spectrum revealed the absence of carbonyl C–O stretching bands.

Characterization Methods. Nanocomposite materials were characterized by using a Philips CM20T transmission electron microscope (TEM) operating at 200 kV. Samples for TEM were prepared by dispersing a powdered sample of nanocomposite onto a 3-mm diameter copper grid covered with amorphous carbon as a substrate. These samples were analyzed with standard bright-field (BF) imaging for particle-size distribution, selected area diffraction (SAD) for their crystal structures, and X-ray energy-dispersive spectroscopy (EDS) for semiquantitative chemical composition. Interpretation of the polycrystalline SAD ring patterns was complicated by the low symmetry of the orthorhombic Co_3C lattice and by the presence of some amount of crystalline Co_3O_4. However, the obtained SAD ring patterns were consistent with the presence of these crystalline structures, and a single-crystal electron diffraction pattern obtained from a single crystalline was successfully indexed using the parameters of the orthorhombic Co_3C lattice.

X-ray diffraction (XRD) scans were obtained using a Philips PW1800 $\theta/2\theta$ automatic powder diffractometer equipped with a Cu target and a post-sample monochromator. Samples for XRD were prepared by placing a uniform layer of powdered nanocomposite onto double-side tape affixed to the sample holder. The sample area was greater than the ca. 1 cm × 1 cm area irradiated by the X-ray beam. Considerable caution was used to keep the top of the sample surface flat and coplanar with the diffractometer rotation axis. To minimize decomposition of the sample by air oxidation prior to analysis by XRD, the sample was flushed with carbon monoxide gas and was then stored under nitrogen.

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer 1600 FT-IR instrument as KBr pellets.

Thermogravimetric analysis (TGA) was performed on a Seiko Instruments TG/DTA 220 instrument. A sample of the molecularly doped xerogel was heated in nitrogen from 25 to 700 °C at a rate of 10 °C/min and from 700 to 900 °C at a rate of 25 °C/min. Sample mass was referenced to that of an empty pan.

Chemical elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Results and Discussion

Addition of the deep purple alkylidynetricobalt nonacarbonyl complex $(HO)_3SiCo_3C(CO)_9$ (**1**) to a conventional sol–gel recipe consisting of a mixture of tetramethylorthosilicate (TMOS), water, methanol, dimethylformamide (DMF), and a catalytic amount of aqueous ammonia gives, after washing with methanol, purple xerogels of variable color intensity depending upon the relative amount of dopant complex used in the synthesis (eq 1). FT-IR spectra of these doped xerogels show a

$$Si(OMe)_4 + \underset{1}{(HO)_3SiCCo_3(CO)_9} \xrightarrow[NH_3\,(aq)\ cat.]{H_2O/MeOH/DMF} SiO_2\ xerogel\ [\equiv SiCCo_3(CO)_x] \quad (1)$$

broad C–O stretching band centered at 2065 cm^{-1} which is consistent with the presence of Co–CO fragments. The corresponding C–O stretching bands for **1** (in CH_2Cl_2 solution)[5] or for $\equiv SiCo_3C(CO)_9$ species attached to the surface of SiO_2 particles[7] are centered at 2058 or at 2060 cm^{-1}, respectively.

Duplicate syntheses of the molecularly doped xerogel using the reported procedure scaled to either 1.36 or 3.41 mmol of TMOS were completed successfully. The initial reactant mole ratio of total Si to Co_3 in both syntheses is 7:1 following this recipe. Chemical elemental analysis of the silicon, cobalt, and carbon content of the two resulting doped xerogel products reveals, respectively, overall ceramic yields of 95 or 98% (based on Si), final Si/Co_3 mole ratios of 8.9:1 or 11.2:1, and final carbon/Co_3 mole ratios of 5.6:1 or 5.3:1. These results indicate (1) the silicon present in both reactants (TMOS and **1**) is essentially completely incorporated into the resulting xerogel, (2) 62–75% of the cobalt initially present as reactant complex **1** becomes incorporated into the doped xerogel product, and (3) a consistently lower than expected carbon content in the resulting xerogel is observed. This latter result is consistent with some degree of chemical decomposition of the cobalt–carbonyl cluster during xerogel formation. Given the known general chemical stability of the core fragment of $RCCo_3(CO)_9$ clusters and the observed retention of the purple color characteristic of these carbidotricobalt clusters, we presume that partial loss of carbon monoxide occurs. Displacement of CO ligands from such complexes has been observed by others and might be expected in this synthesis due to the proximity of the xerogel matrix as **1** becomes covalently incorporated into the xerogel skeleton (vide infra).[8] Schneider and co-workers have observed that the ethylidyne cluster, $MeCCo_3(CO)_9$, is adsorbed onto the surface of silica gels. Exposure of this adsorbate to oxygen leads to loss of carbon monoxide and presumed oxidation of cobalt.[9]

As a control reaction, substitution of **1** by the methylidynetricobalt nonacarbonyl complex, ($HCCo_3(CO)_9$, **2**, a cluster analogous to **1** lacking a trihydroxysilyl functional group) in the synthesis reported above affords a pale green xerogel product that does not show CO stretching bands in the IR spectrum. We conclude that cobalt cluster **2** is not incorporated into the xerogel and is removed completely by washing the xerogel product with methanol. In addition, some amount of **2** apparently undergoes decomposition during xerogel formation

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to give cobalt ion. Reaction of alkylidynetricobalt nonacarbonyl compounds with bases or nucleophiles has been noted by others,[8] so the presence of catalytic amounts of aqueous ammonia in this synthesis could lead to the formation of minor amounts of other reaction products containing cobalt. The results of this control reaction suggest that **1** undergoes covalent incorporation into the silica xerogel through heterocondensation of the Si−OH groups of **1** with those Si−OH groups formed during the hydrolysis of TMOS. While **1** does not undergo facile homocondensation, heterocondensation of **1** with smaller silicate species, such as hexamethyldisiloxane in H_2SO_4/ether solution, has been observed.[5] The extent to which complex **1** undergoes reaction to form cobalt ion species during the gelation process has not been determined.

Samples of undoped xerogel and of xerogel doped with **1** (prepared by the recipe described above) have been analyzed by TGA. The undoped xerogel undergoes a rapid initial weight loss of 11 wt % at temperatures below 150 °C, followed by a much slower weight loss of an additional 5.5 wt % when heated from 150 to 700 °C presumably due to loss of water. When the molecularly doped xerogel is heated at the same rate, a slightly attenuated initial weight loss is observed below 150 °C. Further heating of the doped xerogel from 190 to 400 °C gives a two-stage weight-loss pattern in addition to weight loss due to presumed water expulsion from the xerogel. Within this range, a total weight loss of 10.9% is observed of which a maximum of 2.4 wt % is estimated to be due to loss of water (by comparison to the weight loss observed with the undoped xerogel over the same temperature range). This additional net weight loss of 8.5% is attributed to thermal decomposition of the dopant complex, **1**, with the concomitant evolution of carbon monoxide gas. Chemical elemental analysis of the carbon and cobalt content of the doped xerogel used in the TGA experiment indicates that if all of the carbon present in the xerogel exists solely as Co_3C or as CO, then a 9.0% weight loss is expected from complete expulsion of the carbon monoxide. This prediction corresponds closely to the observed net weight loss of 8.5% and supports the presumption that essentially all of the carbon present in the doped xerogel is located in carbidocobalt carbonyl clusters. Alkylidynetricobalt nonacarbonyl complexes are known to decompose thermally between 100 and 185 °C as pure substances,[8] and **1** is reported to decompose at a temperature greater than 150 °C as a pure material.[5] Worth and co-workers have observed that alkylidynetricobalt nonacarbonyl complexes decompose thermally to give solid, bulk materials having high electrical conductivities.[10] Thermal degradation within the observed temperature range of cluster complexes derived from **1** and possibly stabilized by the xerogel matrix is not unreasonable. A detailed analysis of the thermal decomposition of such cluster compounds within a xerogel environment has not been reported. The presumed two-stage thermal expulsion of carbon monoxide from xerogel doped with **1** has not been investigated further.

When the purple silica xerogel doped with **1** is heated for 2 h at 500 °C in a hydrogen atmosphere, a black xerogel powder is obtained. Chemical elemental analysis of this black xerogel product reveals (1) an increase in the silicon content of the xerogel relative to that of the doped precursor xerogel, and (2) an increase in the Si/Co_3 mole ratio from 11.2:1 to 13.9:1 during the thermal treatment. These results are consistent with retention of silicon and partial loss of cobalt during this pyrolysis under hydrogen, possibly as $HCo(CO)_4$ or as some other volatile species. Upon exposure to air, the black powder slowly turns gray indicating possible air oxidation of a component phase. An FT-IR spectrum of this black product reveals the expected absence of carbonyl ligand C−O stretching bands.

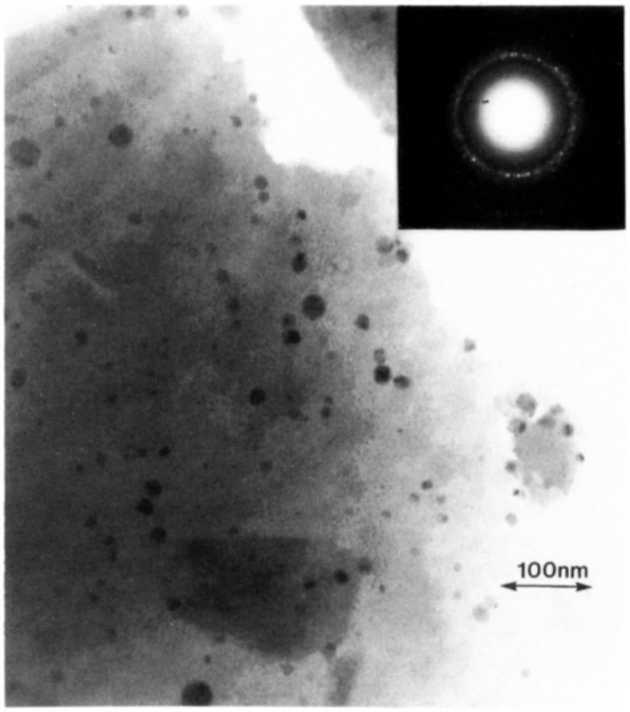

Figure 1. TEM micrograph of a silica xerogel nanocomposite containing nanoclusters of Co_3C. A SAD ring pattern obtained by electron diffraction from the sample is shown as an insert.

A representative TEM micrograph of the black xerogel is shown in Figure 1. Nearly spheroidal particles having diameters in the range 10−46 nm are dispersed throughout the xerogel. A histogram of particle sizes for these particulates shows a monomodal particle-size distribution and an average particle diameter of 25 nm (see Figure 2). An EDS scan of a typical sample of nanocomposite reveals X-ray emissions confirming the presence of silicon and cobalt with relative intensities corresponding to the molar dopant level (see Figure 3). EDS scans of selected on-particle and off-particle areas confirms the concentration of cobalt within the particulate features (see supplementary material).

Electron diffraction from the nanocomposite gives a complex SAD ring pattern which is shown as an insert in Figure 1. Patterns of this complexity would be expected if nanoclusters of crystalline orthorhombic Co_3C were present within the nanocomposite due to the low symmetry of this structure. An observed ring at a d spacing of 2.06 Å is consistent with the (121) reflections ($I/I_0 = 35$) of Co_3C. Furthermore, a dense band of rings is observed within d spacing limits of 1.78−2.18 Å (see Figure 1). Diffraction rings from eight families of reflections of Co_3C [$\{hkl\}$ (I/I_0) = 122 (35), 113 (20), 211 (30), 103 and 022 (100), 210 (35), 121 (35), and 120

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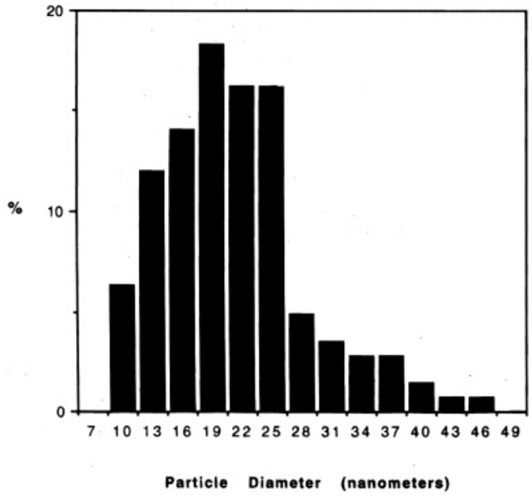

Figure 2. Histogram of nanocluster particle sizes as observed by TEM in a silica xerogel nanocomposite containing nanoclusters of Co_3C.

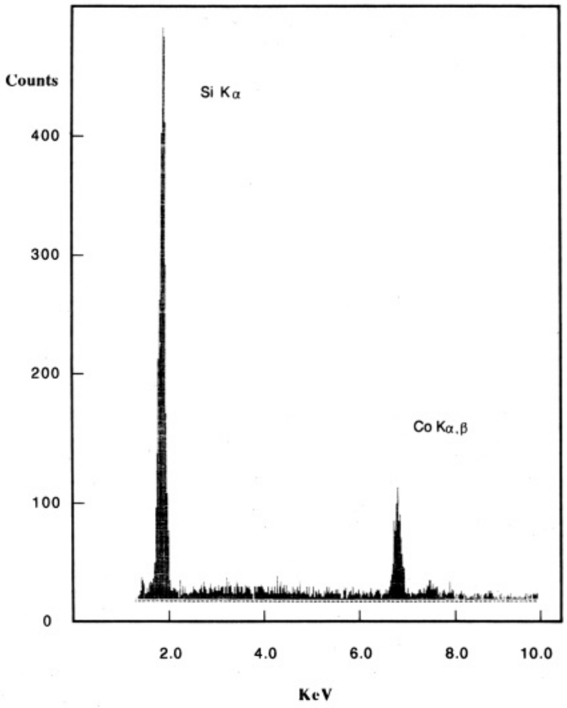

Figure 3. EDS scan of a silica xerogel nanocomposite containing nanoclusters of Co_3C.

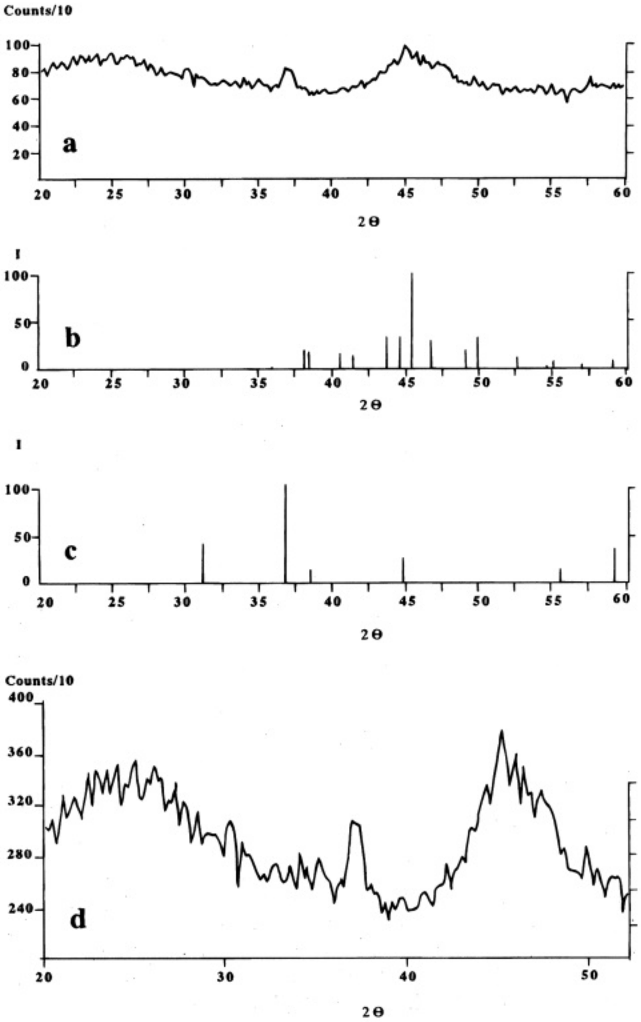

Figure 4. Experimental XRD scan of a silica xerogel nanocomposite containing nanoclusters of Co_3C (a) along with calculated XRD line patterns of orthorhombic Co_3C, (b) and of cubic Co_3O_4 (c). An experimental XRD scan of the nanocomposite sample recorded at expanded scale with better counting statistics is shown in scan d.

(14)] would be expected within this range of *d* spacings, including the ring of greatest relative intensity. Interplanar spacings calculated from the spots obtained in a single-crystal pattern were also consistent with the Co_3C crystal structure (see supplementary material). These electron diffraction data strongly support the presence of Co_3C as the principal crystalline material within the nanocomposite.

An XRD scan of the nanocomposite along with the calculated XRD scans of orthorhombic Co_3C and cubic Co_3O_4 are shown in Figure 4. A broad peak centered at ca. 25° in 2θ arises from amorphous scattering from the silica xerogel host phase as determined through XRD analysis of a sample of undoped xerogel that had undergone similar thermal processing. The most intense peak centered at ca. 45° in 2θ is assigned to several overlapping peaks expected for crystalline Co_3C. The presence of crystalline Co_3O_4 is indicated by the weak peak centered at ca. 37° in 2θ. The low overall intensity of XRD peaks assigned to crystalline Co_3C results from the relatively low doping level of this material and from the low symmetry of this crystalline lattice.

These results support the presence of nanoclusters of crystalline Co_3C dispersed throughout the xerogel matrix of this composite material along with a lesser amount of crystalline Co_3O_4 phase. The presence of cobalt metal or other cobalt carbide structures is not observed. The origin of the Co_3O_4 material is unknown, although oxidation of cobalt could occur during the synthesis of the nanocomposite material or during its subsequent handling prior to analysis by TEM or XRD. The formation of Co_3C nanoclusters is particularly noteworthy given that several cobalt carbide phases are known. This specific cobalt carbide material has the same elemental composition as that of the cluster core of the molecular precursor **1**, and these results suggest that synthetic control of a desired nanostructured material can be achieved through the proper choice of molecular precursor. The extension of this synthetic strategy to the formation of nanocomposites containing nanoclusters of other substances having complex elemental compositions is under investigation.

In related recent work by others, Matteazzi and Le Caer have prepared particulate Co_3C as a bulk material by grinding elemental carbon and cobalt powders at room temperature.[11] Fehlner and co-workers have prepared an effective hydrogenation catalyst from the thermal decomposition of a cobalt oxo cluster containing anionic $(OC)_9Co_3CCO_2$ fragments as ligands.[12] Also, the formation of early transition metal carbides via the decomposition of molecular precursors remains a topic of considerable interest.[13]

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Supplementary Material Available: A summary of the analysis of a single-crystal electron diffraction spot pattern consistent with the cell parameters known for orthorhombic Co_3C and EDS scans of the nanocomposite sample in selected on-particle and off-particle areas (3 pages). Ordering information is given on any current masthead page.

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