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Supplementary Material Available: Listings of calculated atomic coordinates, anisotropic thermal parameters, and nonessential bond lengths and angles (4 pages); listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

Homogeneous Deposition of Palladium(0) into Sol-Gel-Derived Materials

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Using the sol-gel process,[2] solid oxide ceramic materials can be formed that exhibit numerous technologically important optical, mechanical, and electronic properties.[3] Composite materials containing small metal particles dispersed in an oxide matrix have recently attracted much interest for ceramic modification[3] and for the study of small metal colloidal catalysts.[4] Here we report a trialkoxysilane-promoted method for the homogeneous deposition of metal(0) species into sol-gel-derived materials at ambient temperatures during the sol formation process to generate metal particles approximately 15 Å in size. This method for metal(0) deposition should prove to have numerous applications including (1) ceramic modification, (2) supported heterogeneous catalyst preparation, and (3) third-order ($\chi^{(3)}$) nonlinear optical (NLO) enhancement of conjugated organic molecules in monolithic xerogels (precalcinated material) by surface plasmon enhanced Raman scattering.[5]

Metal(0) incorporation into sol-gel-derived ceramic oxides normally involves a four-step sequence including dissolution of the metal salt and $Si(OR)_4$ in an aqueous/organic solvent (ph < 3 or > 9) to allow for the gel formation, drying of the gel to form the xerogel, calcination in air (≥500 °C), and reduction of the metal salt to metal(0) in a hydrogen atmosphere at 300-900 °C.[6,7] The complete reduction of the metal is imperative to ensure homogeneity of the metal(0) species rather than regions of unreduced metal salts. Since reduction takes place after calcination, reduction occurs in the solid (or inhomogeneous melt), and homogeneity of the *metal(0)* can be difficult to obtain. With solid-phase reactions, metal surface reduction can occur without the uniform reduction of the entire particle.[7] Though this classical process is sufficient for many ceramic needs, the high temperatures required for both calcination and reduction to the metal(0) make the development of a milder approach desirable for the synthesis of xerogels containing metal(0).[8]

One distinct advantage in preparing xerogels (rather than calcinated materials) containing metal(0) lies in the ability to prepare novel metal(0), oxide-supported, heterogeneous catalysts. Supported metal catalysts that allow simple separation from the reaction products as well as repeated recycling are the most widely used catalytic systems, and the support is definitely instrumental in modifying the activity of the catalytic metal(0).[4b] These are most often prepared by the deposition of metals onto oxide supports followed by calcination and reduction, but the calcinated oxide material may be far less permeable to reactant molecules than the original xerogel.[2,3] For heterogeneous catalysis, metal(0) in the xerogel would allow the support to remain permeable to organic substrates, and unique catalytic activities should be observable. Accordingly, we recently demonstrated the excellent ability of this palladium-containing gel to act as a chemo- and stereo-

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(8) The term xerogel is used for materials that can readily absorb and desorb water, unlike the final calcinated glass materials. See ref 2a for a detaled explanation.

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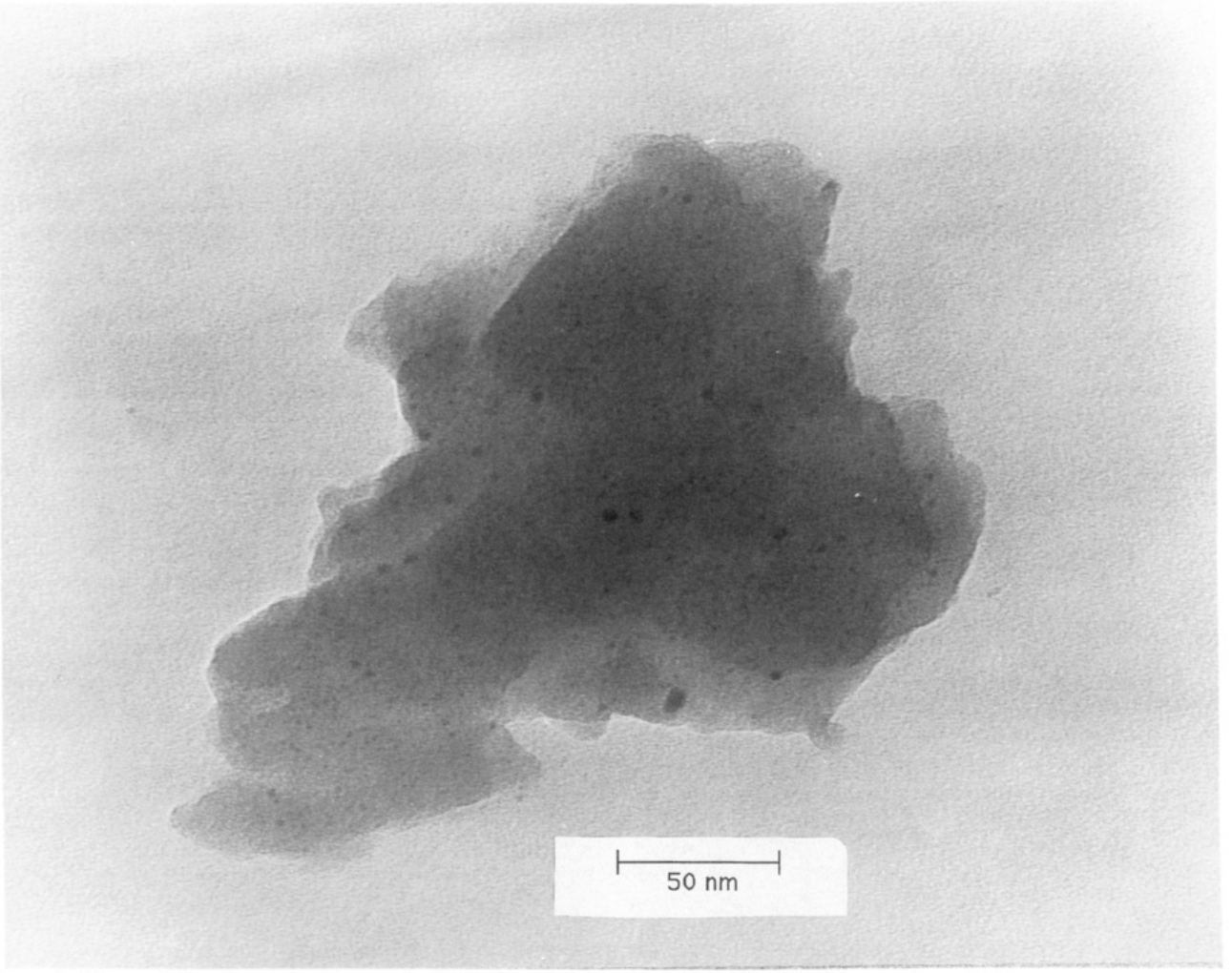

Figure 1. Transmission electron micrograph of Pd(0) containing xerogel. (150 000x, picture enlarged 3×).

selective hydrogenation catalyst. It showed far more selectivity than simply palladium(0) deposited on silica gel.[9]

In the approach described here, treatment of palladium(II) acetate (0.05 mmol) in a mixture of THF (5 mL) and water (1 mL) with triethoxysilane (2.50 mmol) instantly afforded a black solution with the rapid evolution of gas.[10] Both the silane and the hydrogen generated in situ can serve as the reducing source for the palladium.[11] When the reaction was carried out using tetraethoxysilane instead of triethoxysilane, no rapid gas evolution was observed and the solution never darkened to afford the black material. Likewise, in the absence of palladium(II) acetate, the triethoxysilane solutions remained clear. Removal of the solvent in vacuo for 2 days afforded a glossy black xerogel containing palladium(0). An analogous reaction was carried out in water as the only solvent; however, precipitation of the gel occurred within minutes, and hence homogeneous dispersion of the metal(0) species was not as likely to occur as in the THF/water mixtures.

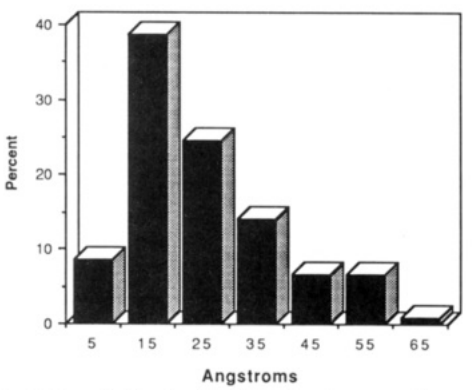

Figure 2. Pd particle size distribution in xerogel.

Mass spectrometric analysis of the vapor above the reaction was monitored during the reaction process. This confirmed that the rapid gaseous evolution was from molecular hydrogen. The elemental (%) composition of the vacuum dried black material is as follows: C, 1.43; H, 1.92; Pd, 0.15; Si, 41.21; O, 55.29. FTIR analysis showed bands at 3479 (O–H, from SiO–H or H_2O, s), 2267 (Si–H, w), 1639 (w), 1084 (Si–O-Si, s), 958 (w), 881 (Si–OH, m), 796 (w) cm^{-1}. Nearly all of the Si–H residue could be consumed, by FTIR analysis, if the reaction were carried out in the presence of an alkyne resulting in reduction of

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the alkyne to the alkene.[9] No absorbances for Si-O-Pd moieties were discernible. However, considering the percentages of Pd in the sample, these could be obscured by the large Si-O absorbances in the 1200-800 cm^{-1} region. Thermogravimetric analysis (TGA) showed 7% weight loss on heating (20 °C/min) to 900 °C. Oven-dried (110 °C, 24 h) samples showed <4% weight loss on heating to 900 °C, which confirms the high degree of cross-linking in the system. Powder X-ray diffraction analysis (XRD) showed no diffraction pattern, signifying that the particles are too small and dispersed to allow a significant repeating unit for the crystallinity determination.[12] However, by doubling the palladium loading, we observed a broad signal (again due to high metal dispersion) for Pd(0) at 2.25 Å. Certainly, further analysis is in order to ensure that smaller, amorphous, or oxide-coated metal salts are not present. No palladium oxide at 2.64 Å or any other Pd crystalline forms were observed. Scanning electron microscopy (SEM) studies using energy-dispersive analysis with X-rays (EDX) indicated that the deposition of palladium is uniform throughout several regions of the polymer studied. Transmission electron microscopy (TEM) showed that the particles were generally on the order of 15 Å in size and uniformly dispersed (Figure 1). A few larger particles, up to ~80 Å, were also detected. A particle size distribution (based on 120 particles) is shown in Figure 2. During the SEM and TEM analysis, much charging of the material occurred. In some samples, particles of palladium in the xerogel were rapidly converging to form larger particles while viewing under the TEM probe. This type of insulator charging during electron field bombardment has recently been addressed.[13]

Finally, in an effort to form sol-gel-derived material containing palladium(0) with no Si-H residue, we have developed a method involving the use of palladium(II) acetate (0.05 equiv), triethoxysilane (0.25 equiv), and tetraethoxysilane (2.5 equiv) in THF/water to afford xerogels that are free from any residual Si-H moiety by FTIR analysis. This is complementary to our system using triethoxysilane and an alkyne for removal of the Si-H residue as discussed previously.

Analysis of the porosity and metal surface area as well as further use of this method for heterogeneous catalyst preparation is being done. Use of this method for the deposition of other metals and mixed-metal composites is currently under investigation for $\chi^{(3)}$ NLO enhancements on monolithic xerogels containing conjugated organic oligomers.

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Reviews

Ladder Polymers: Recent Developments in Syntheses, Characterization, and Potential Applications as Electronic and Optical Materials

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This review covers the syntheses and characterization of ladder polymers exhibiting significant π-electron conjugation. Special emphasis is placed upon discussion of electrical, magnetic, and optical properties and upon the difficulties associated with the synthesis of highly defined structures. Insight is provided into overcoming the problem of polymer solubility that has plagued early research involving ladder polymers.

Introduction

It is well-known that polymers with extensive π-electron conjugation exhibit unusual physical properties.[1,2] Since the observation of metallic conductivities for polyacetylene samples doped with electron donors or acceptors, π-electron polymers have been the focus of an impressive re-

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