In summary, we have developed a new atmospheric pressure CVD process for TiS_2 thin films of high purity, which relies upon the reaction of titanium tetrachloride with volatile organothiols. Several important properties of these coatings (e.g., adhesion, surface finish, density) are superior to those obtained using hydrogen sulfide as the sulfur source. In particular, the crystallographic orientation of the films is ideal for use as cathode materials in lithium batteries. The low carbon content implies that an efficient carbon–sulfur cleavage is operant. Such bond breaking is remarkable in view of the robust nature of carbon–sulfur bonds in thiols (66–74 kcal/mol[15]). The reaction of titanium tetrachloride with organothiols to afford TiS_2 can be contrasted with the thermal decomposition of tetrakis(*tert*-butylthiolato)titanium(IV), which produces TiS coatings.[16] The combined results imply that it may be advantageous to utilize carbon-substituted element precursors in chemical vapor deposition schemes, since our films contained low carbon contamination.[17] We are continuing to work on the delineation of TiS_2 film properties, evaluation of single-source precursors, and titanium–sulfur chemistry of relevance to the CVD processes. These studies will be published in due course.

Acknowledgment. We are grateful to the National Science Foundation (CHE-9123339 to C.H.W.), Ford Motor Co., Glass Division, and the Institute for Manufacturing Research, Wayne State University for financial support. We thank Professor K. Padmanabhan for the RBS spectra, Dr. Umar Riaz for the XPS analyses, and Robert Benoit for the electron microscopy.

Registry No. TiS_2, 12039-13-3; Si, 7440-21-3; *tert*-BuSH, 75-66-1; stainless steel, 12597-68-1.

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Room-Temperature Catalytic Hydrogenation of Aromatic Hydrocarbons Using $[(1,5\text{-COD})RhH]_4$ as a Catalyst Precursor

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There has been intense activity in the synthesis, characterization, and reactivity studies of metal colloids. Metal particles that have sizes in the range 1–50 nm are interesting because they are expected to exhibit unusual catalytic reactivity and selectivity[1] and also quantum confinement effects.[2,3] The typical methods for the preparation of such metal particles are chemical reduction, decomposition of organometallic compounds, and metal atom evaporation to form the so-called small metal atom dispersed (SMAD) catalysts.[4] These materials are often dispersed on high surface area metal oxide supports which aids retention of the dispersion. It has been shown that chemical reduction methods, using $LiBEt_3H$ as reducing agent, can result in the formation of stable colloidal particles in the absence of surfactants in polar organic solvents.[5] Recently, a modification of this approach has been reported using $[NR_4]^+[BEt_3H]^-$, $R = C_8H_{17}$, as a reducing agent, where liberation of a surfactant ($[NR_4]^+$), in situ, resulted in formation of stable colloids containing 1–3-nm-sized metal particles.[6]

We have been interested in developing methods to prepare metal colloids, especially containing rhodium, for catalytic hydrogenation applications.[7–9] In the course of reducing $[(1,5\text{-COD})RhCl]_2$ with $LiBEt_3H$, we observed the formation of $[(1,5\text{-COD})RhH]_4$. This species has been prepared previously by elimination of ethylene from $[(1,5\text{-COD})RhCH_2CH_3]$ above −25 °C,[10] but the reactivity of $[(1,5\text{-COD})RhH]_4$ has not been studied. Here we report the synthesis of $[(1,5\text{-COD})RhH]_4$, its use as a source of 2-nm-sized Rh crystallites under mild conditions, and some preliminary studies of the reactivity of solutions derived from $[(1,5\text{-COD})RhH]_4$ toward the hydrogenation of aromatic hydrocarbons at room temperature.

The compound $[(1,5\text{-COD})RhH]_4$ was prepared by the reaction of $[(1,5\text{-COD})RhCl]_2$ with $LiBEt_3H$ at room temperature in THF under a nitrogen atmosphere.[11] The ^1H NMR characterization data and fluxional behavior were consistent with those reported previously for this compound.[11,12] Solutions of $[(1,5\text{-COD})RhH]_4$ were indefi-

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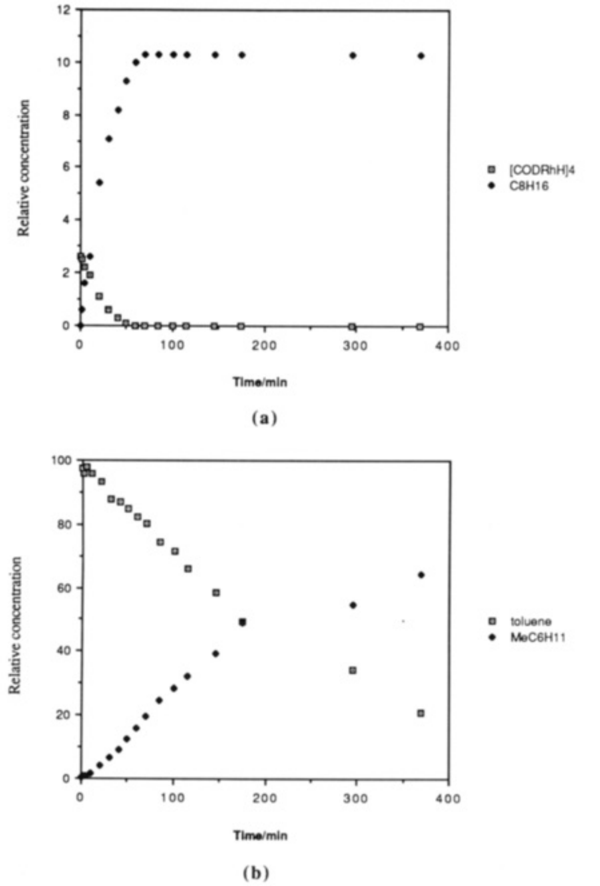

(a)

(b)

Figure 1. Plots of the change in relative concentration of (a) $[(1,5\text{-COD})RhH]_4$ and cyclooctane and (b) toluene and methylcyclohexane as a function of time from the reaction of H_2 with toluene in cyclohexane-d_{12} solution of $[(1,5\text{-COD})RhH]_4$ at room temperature. See ref 13 for details.

nitely stable in aromatic and aliphatic hydrocarbon solvents under inert atmosphere in the absence of hydrogen. However, in the presence of hydrogen, aromatic hydrocarbon solutions of $[(1,5\text{-COD})RhH]_4$ were unstable. When hydrogen was passed through a benzene-d_6 solution of $[(1,5\text{-COD})RhH]_4$ at room temperature, ^1H, ^2H, and ^{13}C (^1H coupled and decoupled) NMR spectroscopic data were consistent with formation of cyclohexane-d_6, and toluene-d_8 was converted to methylcyclohexane-d_8 ($C_6D_5H_6CD_3$). During the reaction a ^1H coupled ^{13}C NMR experiment revealed the presence of aromatic C–*H* bonds consistent with either dehydrogenation of the product or H/D exchange between $[(1,5\text{-COD})RhH]_4$ and the aromatic hydrocarbon. Dissolution of $[(1,5\text{-COD})RhD]_4$ in C_6H_6 resulted in a slow increase in the intensity of the hydride resonance with time, indicating H/D exchange is possible but slower than for the ^1H NMR time scale at 250 MHz.

To provide further insight into the role of $[(1,5\text{-COD})RhH]_4$ in these reactions, the hydrogenation of toluene was studied in more detail. Toluene was chosen because the methyl group in the starting material and product were convenient to monitor by ^1H NMR spectroscopy and are clearly distinguishable and because the methyl groups retain their integrity during the reaction (i.e., negligible H/D exchange) as shown by the hydrogenation of toluene-d_8 described above. Toluene and $[(1,5\text{-COD})RhH]_4$ were dissolved in cyclohexane-d_{12} in a molar ratio of 154:1, and the changes in the integration ratio of the ^1H NMR resonances ascribed to toluene, $[(1,5\text{-COD})RhH]_4$, cyclooctane, and methylcyclohexane were monitored as a function of time while hydrogen was passed through the solution.[13] The identity of these products were confirmed by GC-MS.[14] The results of this experiment are shown in Figure 1. The concentration of $[(1,5\text{-COD})RhH]_4$ slowly decreased to zero after 60 min with a concomitant increase in the concentration of cyclooctane as shown in Figure 1a. The rate of decrease of $[(1,5\text{-COD})RhH]_4$ concentration and the rate of increase of cyclooctane concentration followed first-order kinetics. The rate of loss of toluene should be equal to the rate of formation of methylcyclohexane, and this is observed for the first 175 min (see Figure 1b). At longer times, the slopes of these plots changed, indicating a decrease in the reaction rate. From the linear portions of the plots, a reaction rate of 1.83×10^{-3} molecules of toluene converted/(Rh atom (total) s) was calculated, which compares favorably with the literature rate data for the heterogeneous hydrogenation of benzene of 9.6×10^{-4} molecules of benzene/(Rh atom s) for an Al_2O_3-supported Rh catalyst.[15] These values are

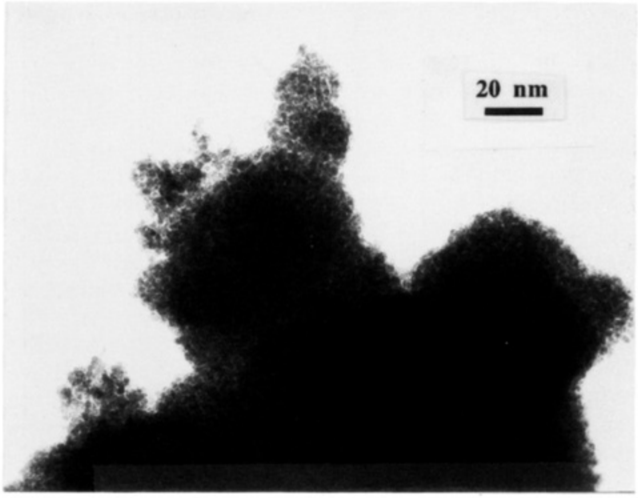

Figure 2. TEM data for the solid obtained from the reaction of H_2 with toluene in cyclohexane-d_{12} solution of $[(1,5\text{-COD})RhH]_4$ at room temperature.

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(13) The hydrogenation of toluene on cyclohexan-d_{12} was carried out several times in 5- and 10-mm NMR tubes using a Bruker AC-250P, and the changes in concentration were monitored by ^1H NMR (250.13 MHz) integration of the relative intensities of the peaks. The concentrations were monitored as follows: toluene by the methyl resonance (singlet, 2.01 ppm); $[(1,5\text{-COD})RhH]_4$ by the olefinic 1,5-COD resonance (singlet, br, 4.79 ppm); cyclooctane by its single resonance (singlet, 1.54 ppm); methylcyclohexane by the methyl resonance (doublet, 0.87 ppm) after subtraction of the underlying CH and half of a CH_2 resonance. A typical reaction involved dissolution of 0.0523 g (0.0616 mmol) of $[(1,5\text{-COD})RhH]_4$ in 1.0 mL (9.41 mmol) of toluene and 2.0 mL of cyclohexane-d_{12}. Hydrogen was passed through the solution, and ^1H NMR was measured at various times.

(14) GC-MS data showed the presence of four components after the hydrogenation experiment had continued for 370 min. The first component exhibited a retention time of 2.32 min, with mass spectral data corresponding to cyclohexane-d_{12}, C_6D_{12}, as follows: $m/z = 96$, $C_6D_{12}^+$, 100%; 78, $C_5D_9^+$, 26%; 64, $C_4D_8^+$, 67%; 62, $C_4D_7^+$, 18%; 46, $C_3D_5^+$, 17%. The second component exhibited a retention time of 3.1 min with mass spectral data corresponding to cyclooctane, C_8H_{16}, as follows: $m/z = 112$, $C_8H_{16}^+$, 100%; 84, $C_6H_{12}^+$, 20%; 83, $C_6H_{11}^+$, 46%; 70, $C_5H_{10}^+$, 47%; 69, $C_5H_9^+$, 37%; 56, $C_4H_8^+$, 57%; 55, $C_4H_7^+$, 34%. The third component exhibited a retention time of 3.4 min, with mass spectral data corresponding to methylcyclohexane, C_7H_{14}, as follows: $m/z = 98$, $C_7H_{14}^+$, 68%; 83, $C_6H_{11}^+$, 100%; 82, $C_6H_{10}^+$, 17%; 70, $C_5H_{10}^+$, 17%; 69, $C_5H_9^+$, 18%; 56, $C_4H_8^+$, 15%; 55, $C_4H_7^+$, 42%. The fourth component exhibited a retention time of 4.45 min with mass spectral data corresponding to toluene, C_7H_8, as follows: $m/z = 92$, $C_7H_8^+$, 66%; 91, $C_7H_7^+$, 100%. The last three components, cyclooctane (C_8H_{16}), methylcyclohexane (C_7H_{14}), and toluene (C_7H_8), exhibited mass spectral fragmentation patterns consistent with the literature data.

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Chem. Mater. **1992,** *4,* 1148–1150

also comparable with heterogeneous benzene hydrogenation catalyzed by 0.1 wt % Rh (derived from $RhCl_3$) on silica with a turnover frequency of approximately 10^{-3} molecules of benzene/(surface Rh atom s).[7] The most notable feature of these graphs is that the hydrogenation of toluene continued well past the time at which all the $[(1,5\text{-COD})RhH]_4$ had been consumed. From these data it appears that the hydrogenation reaction was not stoichiometric in Rh concentration, and $[(1,5\text{-COD})RhH]_4$ derived solutions were capable of at least 127 turnovers, after which the experiment was stopped. The compound $[(1,5\text{-COD})RhH]_4$ may be responsible for some catalytic hydrogenation. If it were not an active catalyst, the rate of toluene hydrogenation should increase as the active catalyst is formed and then become constant after all the $[(1,5\text{-COD})RhH]_4$ is consumed. Qualitatively, this appears not to be the case, but the data are not unambiguous in this respect. However, this species must be a precursor to an active hydrogenation catalyst since the hydrogenation activity continues long after the $[(1,5\text{-COD})RhH]_4$ was reacted.

During addition of hydrogen to $[(1,5\text{-COD})RhH]_4$ solutions, a black solid was precipitated and the initial dark red solution became colorless after 60 min, when all the $[(1,5\text{-COD})RhH]_4$ had been consumed. The black solid was isolated and shown to be comprised of agglomerated ~2-nm-sized particles of crystalline rhodium as determined by transmission electron microscopy, energy-dispersive spectroscopy, and electron diffraction (see Figure 2). X-ray powder diffraction experiments could not distinguish between an amorphous material and crystalline rhodium with a small crystallite size. However, the position (2θ) and width of the X-ray diffraction peaks observed at room temperature were consistent with the presence of 2-nm-sized crystallites. On heating this solid to 400 °C, sharp X-ray diffraction peaks were observed at positions that corresponded to the presence of crystalline rhodium. A particle size of 2 nm corresponds to a turnover frequency of 2.3×10^{-3} molecules of toluene/(*surface* Rh atom s).

Preliminary studies of the hydrogenation activity of functionalized aromatic hydrocarbons exhibited quite different behavior. Pyridine-d_5 was not hydrogenated on the same time scale that hydrogenation of benzene-d_6 and toluene-d_8 was observed, but instead, D/H exchange was observed selectively into the *o*-phenyl position as determined by ^{1}H NMR spectroscopy. Furthermore, benzophenone (and acetone) did not react on the same time scale as benzene-d_6 and toluene-d_8, although $[(1,5\text{-COD})RhH]_4$ was converted to Rh metal in every case. In a competition experiment, a mixture of benzophenone and toluene were dissolved in a cyclohexane-d_{12} solution of $[(1,5\text{-COD})RhH]_4$. The rate of hydrogenation of toluene was severely depressed under these conditions. No methylcyclohexane was formed after 120 min. This indicated that the benzophenone probably poisoned the catalytically active sites perhaps via coordination of the carbonyl functionality. Coordination of the nitrogen lone pair of pyridine-d_5 to the catalyst might also explain the observed ortho deuterium D/H exchange as a result of their proximity to the active site(s).

The interaction of toluene with condensed metal vapors has been postulated to result in formation of π-toluene complexes.[1,16,17] The species derived from the condensation of Rh vapor into toluene was found to be an active hydrogenation catalyst for the conversion of toluene to methylcyclohexane.[18] An analogous species may be formed as an intermediate in these reactions. Further studies are in progress to determine the stereochemistry and selectivity of hydrogenation of aromatic hydrocarbons with $[(1,5\text{-COD})RhH]_4$ and to develop the strategy of the removal of alkene ligands from metal–organic complexes to liberate small metal clusters under mild conditions.

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Registry No. $LiBEt_3H$, 22560-16-3; $[(1,5\text{-COD})RhCl]_2$, 12092-47-6; $[(1,5\text{-COD})RhH]_4$, 82660-97-7; $LiBEt_3D$, 74540-86-6; $[(1,5\text{-COD})RhD]_4$, 144001-68-3; $C_6D_5H_6CD_3$, 144001-67-2; Rh, 7440-16-6; H_2, 1333-74-0; benzene-d_6, 1076-43-3; cyclohexane-*1,2,3,4,5,6*-d_6, 144001-66-1; toluene-d_8, 2037-26-5; toluene, 108-88-3; methylcyclohexane, 108-87-2; pyridine-d_5, 7291-22-7.

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Poled Polymeric Nonlinear Optical Materials. Exceptional Second Harmonic Generation Temporal Stability of a Chromophore-Functionalized Polyimide

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Rational synthetic approaches to efficient polymeric second-order nonlinear optical materials[1] must address the crucial requirements of maximizing constituent chromophore number densities while achieving and preserving maximum microstructural accentricity. Acceptable thermal environments must ultimately include those of device fabrication as well as prolonged use. To these ends, poled cross-linkable chromophore-functionalized glassy polymers[2,3] and poled matrices based upon cross-linkable

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