Synthesis and Characterization of Nanophase Group 6 Metal (M) and Metal Carbide (M_2C) Powders by Chemical Reduction Methods

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The group 6 metal chlorides $CrCl_3$, $MoCl_3$, $MoCl_4$ and WCl_4 were reduced in *toluene* solution with $NaBEt_3H$ at room temperature to form the corresponding metal colloids in high yield. When the same metal chlorides were reduced in *THF* solution with $LiBEt_3H$ and $NaBEt_3H$, metal carbides (M_2C) were formed in approximately 95% yield. The metal and metal carbide colloids were shown to be comprised of 1–5-nm-sized particles by TEM. The metal and metal carbide powders derived from the colloids by centrifuging and washing with various solvents were characterized with SEM, TEM, EDS, and ED which showed that the powders were comprised of agglomerates of the primary 1–5-nm-sized crystallites. X-ray powder diffraction studies of these black powders exhibited broad peaks for the as-prepared powders at room temperature where the crystallite size estimated from the broadening analysis generally corresponded to the primary particle size as determined by TEM. Variable-temperature X-ray powder diffraction allowed unambiguous identification of the crystalline metal and metal carbide phases present. Carbon and hydrogen combustion elemental analysis was also used to identify the metal and metal carbide materials. Thermogravimetric analysis in air provided information on the oxidation behavior of these materials and also enabled distinction between the formation of metals versus metal carbides, M_2C. Experiments to determine the exact origin of the carbide carbon were inconclusive. Treatment of nanocrystalline W with THF and THF/$LiBEt_3H$ solutions did not result in further reaction to form the metal carbide.

Introduction

Nanometer-sized particles of a wide variety of materials that exhibit electrical conductivity, semiconductivity, and magnetic phenomena are generating a great deal of interest. Modification of their bulk properties due to their small dimensions results in so-called quantum-confinement effects.[1–3] In addition, nanometer-sized particles of metals and metal oxides are of interest for catalysis applications[4] and in materials science to promote solid-state reactions where high surface area and therefore high surface energy often result in low-temperature solid-state reactions.[5] A large variety of synthetic techniques have been used to prepare materials composed of nanometer-sized particles, including vapor-phase methods such as physical vapor deposition (PVD),[6] metal atom vaporization,[7] chemical vapor deposition (CVD),[8] or aerosol-assisted deposition[9] and liquid-phase methods including, controlled hydrolysis,[10] sol–gel chemistry,[11] spray pyrolysis,[9] and chemical reduction reactions.[12] In general, solid-state synthesis and processing techniques are not viable methods for the formation of nanophase materials either due to the inability to form nanometer-sized particles or as a result of the introduction of impurities on grinding and sintering.[13]

Homogenous liquid phase chemical reduction methods have been used to form nanometer-sized metal particles. The introduction of surfactants is often necessary to control particle size in micelles but can result in contamination of the surface of the final materials which is often detrimental to their subsequent reactivity.[14] However, in the absence of surfactants, highly reactive metal particles can be formed. Noble-metal particles can be prepared using mild reducing agents such as alcohols.[15] The salts of more electropositive metals require stronger reducing agents such as alkali metals and can be reduced either heterogeneously[12] or in homogeneous solution by dissolving

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the alkali metal in a polar solvent in the presence of an electron carrier such as naphthalene.[12] Nanoscale metal particles have also been prepared by homogeneous reduction of metal salts using alkalides and electrides.[16] Rieke et al.[17-19] and others[20] have prepared highly reactive metal particles by the reduction of metal halides according to the example shown in eq 1. In an alternative approach,

$$MgX_2 + 2K \rightarrow Mg + 2KCl \qquad (1)$$

Boennemann et al.[21,22] have used trialkylborohydride reducing agents such as $MBEt_3H$ (M = Li, Na, or K) to reduce a variety of metal halides in organic solvents which result in formation of metal particles. More recently, we have communicated our initial observation that the reduction of $MoCl_3(THF)_3$ with $LiBEt_3H$ in THF results in formation of the highly dispersed nanophase molybdenum carbide Mo_2C, rather than the corresponding metal.[23] Here we report more extensive studies of these reactions in which the metal halide, solvent and reducing agent are varied and show that depending on the nature of the solvent either metal or metal carbides are formed in these reduction reactions.

Experimental Section

General Procedures and Instrumentation. All manipulations were carried out under a dinitrogen atmosphere using standard Schlenk techniques[24] due to the oxygen and moisture sensitivities of the starting materials and the pyrophoric nature of the crude metal and carbide powders. $CrCl_3$ (Aldrich), $MoCl_3$ (Aldrich) and WCl_4 (Aldrich) were used as purchased. $MoCl_3(THF)_3$ and $MoCl_4(THF)_2$ were prepared by diphenylsilane reduction of $MoCl_5$ as previously reported.[25] Tetrahydrofuran was predried over sodium and distilled from sodium benzophenone ketyl and was stored over 4-Å molecular sieves. Methanol was distilled from calcium hydride and was stored over 4-Å molecular sieves. The 1.0 M tetrahydrofuran solution of lithium triethylborohydride and sodium triethylborohydride and 1.0 M toluene solution of sodium triethylborohydride (Aldrich) were all used as purchased. Combustion element analyses were performed by Ms. R. Ju in the Department of Chemistry at the University of New Mexico with use of a catalytic combustion agent such as WO_3 where necessary. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA 7 instrument. Scanning electron microscopy (SEM) was obtained with a Hitachi S-800 instrument. Transmission electron microscopy (TEM) was performed on a JEOL 2000-FX instrument operating at 200 keV. Both SEM and TEM samples were prepared by redispersing the black powder formed as reaction product in the appropriate solvent, toluene for metals, tetrahydrofuran for metal carbides, to form a black suspension from which a silicon wafer could be dip-coated for SEM or a 3-mm carbon-coated copper grid could be dip-coated for TEM. X-ray powder diffraction data was collected on the PVD-V Scintag X-ray diffractometer using a smear mount method to load a uniform and thin layer of sample onto a piece of glass of size 3 × 3 cm^2. Thermal annealing for the product was carried out on a scale of approximately 20–40 mg by placing the black powder in a quartz boat inside a quartz furnace tube with both ends capped under dinitrogen atmosphere. The tube was loaded into a tube furnace, evacuated to 10^{-2} Torr, and heated slowly to the specific temperature for the desired length of time.

Synthesis of Metal Powders by $NaBEt_3H$ Reduction of MCl_n in Toluene Solution. (*i*) *Cr*: Chromium trichloride, $CrCl_3$ (3.00 g, 18.93 mmol) was suspended in 70 mL of toluene forming a purple suspension. Into this suspension, 60 mL of a 1.0 M toluene solution of sodium triethylborohydride was added dropwise at room temperature while stirring. Slow gas evolution was observed. After stirring for 48 h at room temperature, a black suspension was formed. The black suspension was then centrifuged to give a black precipitate and a colorless clear solution. The black solid was washed with toluene and pentane and pumped dry to give 4.26 g of black powder. At this stage, no attempt was made to remove the sodium chloride byproduct. The yield based on formation of Cr + 3NaCl was 99%. Elemental analysis calcd for Cr·3NaCl: C, 0%; H, 0%. Found: C, 0%; H, 0%.

(*ii*) *Mo*: Molybdenum trichloride, $MoCl_3$ (4.12 g, 20.35 mmol) was suspended in 75 mL of toluene. Then, 72 mL of a 1.0 M toluene solution of sodium triethylborohydride was added slowly at room temperature while stirring. Gas evolution was observed and the color deepended to give a black suspension after stirring for 48 h at room temperature. The black suspension was centrifuged to give a black precipitate and a colorless solution. The black precipitate was washed with toluene and pentane and then pumped dry to give 5.41 g of product. At this stage, no attempt was made to remove the sodium chloride byproduct. The yield based on formation of Mo + 3NaCl was 98%. Elemental analysis calcd for Mo·3NaCl: C, 0%; H, 0%. Found: C, 0.98%; H, 0%.

(*iii*) *W*: Tungsten tetrachloride, WCl_4 (6.08 g, 18.65 mmol) in toluene (100 mL) was treated with a 1.0 M toluene solution of sodium triethylborohydride (75 mL). Slow gas evolution was observed and a black suspension was formed after continued stirring at room temperature for 48 h. The black suspension was centrifuged to separate the black solid product from the colorless solution. After washing with toluene and pentane, the black solid was pumped dry to give 7.66 g of black powder product, A yield of 94% was determined based on the presence of all the sodium chloride byproduct, W + 4NaCl. Elemental analysis calcd for W·4NaCl: C, 0%; H, 0%. Found: C, 0.41%; H, 0%.

(c) Synthesis of W_2C by $NaBEt_3H$ Reduction of WCl_4 in THF. A 1.0 M THF solution of sodium triethylborohydride (76 mL) was added dropwise to a black THF suspension of tungsten tetrachloride (6.00 g, 18.40 mmol) at room temperature while stirring. Immediate gas evolution and color changes from black to coffee-brown, dark blue, and finally black were observed. The reaction mixture was stirred for 36 h to form a homogeneous black suspension which was centrifuged to precipitate a black solid. The black solid was washed with methanol and THF and then dried *in vacuo* to give a black powder. At this stage, no attempt was made to remove the sodium chloride byproduct. The yield based on formation of W_2C + 8NaCl of 7.48 g was 96%. Elemental analysis calcd for W_2C·8NaCl: C, 1.42%; H, 0%. Found: C, 3.49% H, 0.24%.

In a separate experiment, the initial crude product was washed with the deoxygenated water followed by washing with methanol and THF, and the black powder was pumped dry to give quantitative formation of W_2C. Elemental analysis calcd for W_2C: C, 3.2%; H, 0%. Found: C, 2.5%; H, 0.4%.

(d) Synthesis of Metal Carbides by $LiBEt_3H$ Reduction of MCl_n in THF. (*i*) *Cr_2C*: Chromium trichloride, $CrCl_3$ (5.00 g, 31.55 mmol) was suspended in 100 mL of tetrahydrofuran forming a purple suspension. A 1.0 M tetrahydrofuran solution of lithium triethylborohydride (95 mL) was then added dropwise to the $CrCl_3$ suspension while stirring at room temperature. Gas evolution was observed immediately. The color changed initially from purple to green and then to gray. After one-third of lithium triethylborohydride was added, a white solid was formed. On continued addition of the remaining lithium triethylborohydride, the white suspension changed to a black suspension. After stirring for a total of 24 h, the black suspension was centrifuged at 2000 rpm for approximately 30 min to separate a black solid. The

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black solid was washed with 100 mL of THF, 100 mL of methanol, and a 100 mL of a mixture of THF and methanol (1:1 by volume) until no further bubbling was observed. The black solid was washed again with THF and was pumped dry to give a quantitative yield of black powder. Elemental analysis calcd for Cr_2C: C, 10.34%; H, 0%. Found: C, 5.48%; H, 1.21%; N, 0.89%.

(*ii*) *Mo_2C*: Trichlorotris(tetrahydrofuran)molybdenum, $MoCl_3(THF)_3$ (6.03 g, 14.41 mmol) was suspended in 150 mL of THF and then cooled by an ice/NaCl/H_2O cooling bath (~−10 °C). Into this suspension, 50.0 mL of 1.0 M $LiBEt_3H$/THF was added by syringe. An immediate color change from red-brown to black accompanied by a gas evolution was observed. After stirring for 24 h at room temperature, the black suspension was centrifuged to precipitate the black solid which after washing with THF, and an ethanol/THF mixture, was dried *in vacuo*. The reaction gave a 93% yield of Mo_2C. Elemental analysis calcd for Mo_2C: C, 5.88%; H, 0%. Found: C, 6.43; H, 1.07%.

The reduction of $MoCl_4(THF)_2$ with 4 equiv of 1.0 M $LiBEt_3H$/THF was performed under the same conditions to yield a black powder with elemental analysis of C, 6.32%; H, 1.04%.

(*iii*) *W_2C*: Tungsten tetrachloride, WCl_4 (4.20 g, 12.88 mmol) was suspended in 100 mL of THF which was cooled by ice/NaCl/H_2O cooling bath. Then, 60 mL of 1.0 M $LiBEt_3H$ in THF was added by syringe while stirring. Immediate gas evolution and a deepened black color was observed. After stirring overnight at room temperature, a black suspension was formed and black precipitate was separated by centrifugation. The black precipitate was washed with THF, EtOH, and THF and pumped dry to yield 95% of W_2C. Elemental analysis calcd for W_2C: C, 3.2%; H, 0%. Found: C, 5.9%; H, 1.0%.

(e) Experiments To Investigate the Role of the Solvent and Reducing Agent on the Nature of the Product (W vs W_2C). The reagent WCl_4 (3.26 g, 10.00 mmol) was suspended in 75 mL of toluene. A toluene suspension of 1.0 M sodium triethylborohydride (45.0 mL, 45.00 mmol) was then added to the suspension at room temperature while stirring. Slow gas evolution was observed and reaction was stirred for 48 h, leading to formation of black colloidal solution. The colloidal solution was centrifuged at room temperature to isolate the black solid. After washing with 80 mL of toluene and 80 mL of pentane and drying *in vacuo*, 3.90 g of black powder was obtained, a 93% yield based on the presence of all sodium chloride byproduct, W + 4NaCl. This powder was then used for the following experiments.

(1) The black powder (50 mg) was annealed at 500 °C for 4 h, and X-ray diffraction showed presence of only nanocrystalline W metal in addition to crystalline NaCl (see Figure 10a).

(2) The black powder (1.8 g) was suspended in THF (50 mL) and stirred at room temperature for 24 h to form a black suspension. (2a) 25 mL of the suspension obtained from (2) was centrifuged and dried under vacuum to give 0.9 g of black powder. The powder was then annealed at 500 °C for 4 h. X-ray diffraction of the annealed material showed nanocrystalline W metal and crystalline NaCl (see Figure 10b). (2b) The remaining suspension obtained in (2) was treated with 18 mL of a THF solution of 1.0 M lithium triethylborohydride for 24 h. The suspension was then centrifuged and washed with 50 mL of ethanol, 50 mL of THF, and then dried under vacuum to give 0.8 g of black powder which was annealed for 4 h under vacuum. X-ray diffraction of the annealed product was shown to be nanocrystalline W metal together with crystalline NaCl (see Figure 10c).

Results and Discussion

(1) Synthesis of Metal Powders by $NaBEt_3H$ Reduction of MCl_n (M = Cr, Mo, and W) in Toluene. The reduction of the metal halides, MCl_n, $n = 3$ or 4, in toluene with a slight excess of sodium triethylborohydride for 2 days resulted in gas evolution and yielded a black powder which was separated from the solution by centrifuging. In initial experiments, no attempt was made to remove the NaCl produced as byproduct because it was anticipated that addition of water might result in either reaction with the product or a change in microstructure.

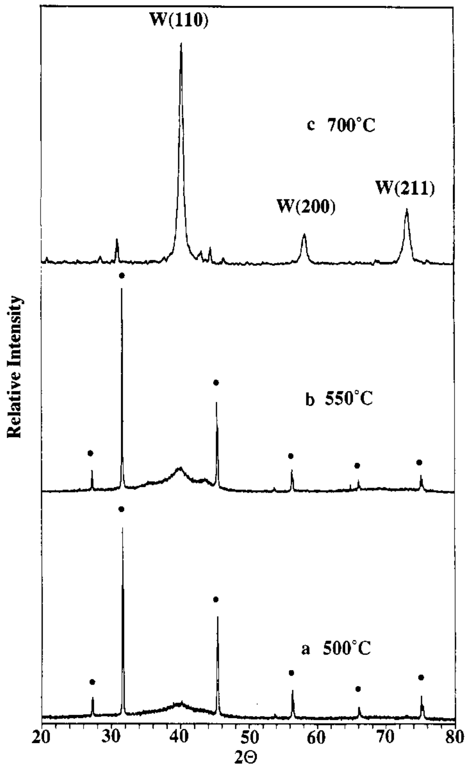

Figure 1. X-ray powder diffraction data obtained after heating the powder isolated from the reduction of WCl_4 in toluene to 500, (a), 550, (b) and 700 °C (c) for 4 h each *in vacuo*. The peaks labeled (●) correspond to NaCl, the remaining peaks correspond to W.

In the case of M = Cr, the black powder was found to contain Cr and crystalline NaCl by energy dispersive spectroscopy and X-ray powder diffraction. The formation of Cr metal rather than chromium carbide, Cr_2C (see later), was confirmed by combustion elemental analysis in which no carbon was detected. An X-ray diffraction pattern of the sample after heating to 500 °C for 4 h exhibited a broad peak centered at a *d* spacing of 2.05 Å in addition to the crystalline NaCl peaks. Although the most intense peaks for Cr [(210), *d* spacing = 2.05 Å] and Cr_2C [(101), *d* spacing = 2.11 Å] exhibit similar *d* spacing, the two phases could be distinguished.

Similar results were obtained on reduction of $MoCl_3$ by sodium triethylborohydride in toluene. Molybdenum metal was formed rather than Mo_2C powder based on X-ray powder diffraction data after heating to 500 °C for 4 h as determined by the position of the most intense X-ray diffraction peaks for Mo [(110), 2.25 Å] and Mo_2C [(101), 2.28 Å]. In this case, elemental analysis showed that this sample contained a small amount of carbon, but a significantly smaller amount than would be expected for Mo_2C.

When WCl_4 was reduced by sodium triethylborohydride in toluene, metallic tungsten was formed rather than W_2C. The black powder contained a small amount of carbon, 0.41%, less than the expected for W_2C. The results of a series of X-ray diffraction experiments after heating this sample to various temperatures are shown in Figure 1. The sample was heated to 500, 550, and 700 °C for 4 h each *in vacuo*. As the temperature increased, the X-ray diffraction peaks sharpened and the peaks observed were consistent with tungsten metal. At higher temperatures, the NaCl impurity sublimed. There was no evidence for the presence of W_2C.

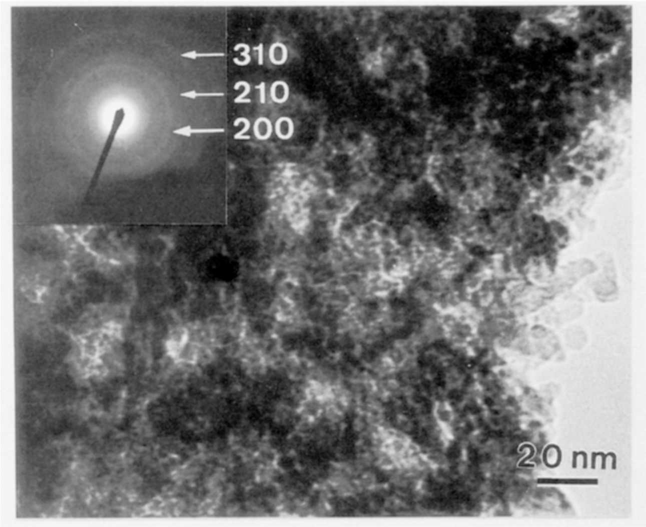

Figure 2. TEM micrograph and electron diffraction data for Cr powder heated to 500 °C *in vacuo.*

The morphology, particle size, and crystallite sizes of all three powders were investigated by SEM, TEM, and electron diffraction. These experiments revealed that the primary particle size was analogous to that determined by the broadening of the X-ray diffraction peaks according to the Scherrer equation.[26] An example of the TEM data for the Cr powder heated to 500 °C *in vacuo* is shown in Figure 2. The electron diffraction pattern shows diffuse rings that have *d* spacings consistent with the expected positions of the most intense peaks for the lattice spacings of Cr metal. In general the powders were isolated as agglomerates of these primary crystallites with dimensions of approximately 400–500 nm as determined by SEM.

Initially these powders were characterized with the NaCl byproduct intact. However, when the as-precipitated black powders were washed with the deoxygenated water the NaCl could be removed without observable oxidation of the metal as determined by X-ray diffraction or a change in the microstructure as determined by SEM and TEM. TGA of the water washed sample in air showed the conversion of W to W_2O_5 at 350 °C, based on a comparison of the calculated (22%) and observed (22%) weight gain, consistent with the presence of tungsten metal after deoxygenated water treatment. Thermal oxidation at higher temperatures (~800 °C) resulted in formation of crystalline WO_3 as determined by X-ray powder diffraction.

The proposed equation for the reduction reaction is given below, eq 2, generalized for M = Cr, and Mo, $x = 3$ and M = W, $x = 4$. This reaction either may result from direct

$$MCl_x + xNaBEt_3H \xrightarrow{\text{toluene}} M + xNaCl + xBEt_3 + (x/2)H_2 \qquad (2)$$

hydride transfer to form a metal hydride intermediate which subsequently reductively eliminates H_2 or may be reduced directly by an electron-transfer mechanism. These possibilities have been rationalized[21] previously in terms of hard/soft acid/base theory.[27] The possibility that stoichiometric metal carbides were formed was ruled out by elemental analysis and a comparison of the X-ray powder diffraction data. Although the X-ray powder diffraction data for the metal carbides, M_2C, M = Cr, Mo, and W are very similar to those of the corresponding metals as a result of the small change in lattice parameters between the two,[28] the differences are sufficient that the two phases can be distinguished even when the crystallites size is on the order of only a few nanometers. A comparison of the X-ray powder diffraction data for the nanocrystalline products of the reduction of WCl_4 in toluene to form W and in THF to form W_2C (see later) are presented in Figure 3. This comparison clearly shows that the broad peaks have different maxima. In all cases, reduction in toluene solution followed by isolation by centrifuging resulted in formation of agglomerates of small, 2–4-nm-sized crystallites which grew on heating to 500–700 °C (see Figure 1).

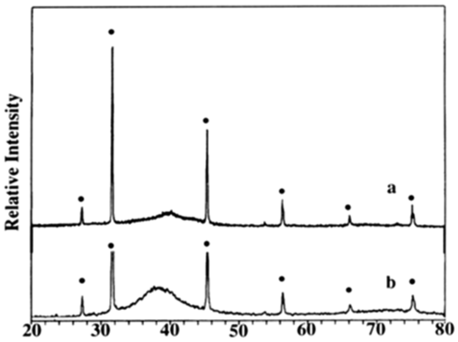

Figure 3. Comparison of the XRD data for powders prepared from the reduction of WCl_4 in toluene (a) versus THF (b) emphasizing the difference in the position of the peak maximum for W (110) and W_2C (101). The peaks marked by ● are due to the presence of NaCl.

(2) Synthesis of W_2C by $NaBEt_3H$ Reduction of WCl_4 in THF. The reduction of WCl_4 with sodium triethylborohydride in THF also resulted in formation of a black powder. However, the characterization data were consistent with formation of W_2C rather than W in this case where THF was used as the reaction solvent. In the crude reaction products, the elements W, Na, and Cl, were shown to be present by energy-dispersive spectroscopy (the instrument is not sensitive to the presence of light elements including C) and X-ray powder diffraction revealed the presence of the crystalline phases W_2C and NaCl. Room-temperature X-ray diffraction of this product showed mainly crystalline NaCl and a very broad diffraction peak centered at ca. 2.3 Å (Figure 4a). This sample was annealed at 500 °C for 4 h, and the X-ray diffraction still showed only a very broad peak centered at ca. 2.3 Å (Figure 4b). However, when product was heated to 650 °C for 4 h, the most intense diffraction peak due to the W_2C, (101) was found at *d* spacing of 2.29 Å as shown in Figure 4c, in contrast to the value for the most intense diffraction peak from W, (110), which is at a *d* spacing of 2.24 Å (see Figure 3).

In a separate experiment, the crude product was washed with water to remove the NaCl. It was found that W_2C completely oxidizes to form WO_2, as shown by the X-ray powder diffraction, when nondeoxygenated water is used. However, NaCl can be completely removed from W_2C without observable oxidation products in the X-ray powder diffraction pattern if deoxygenated water is used. The overall morphology of the W_2C powder was virtually

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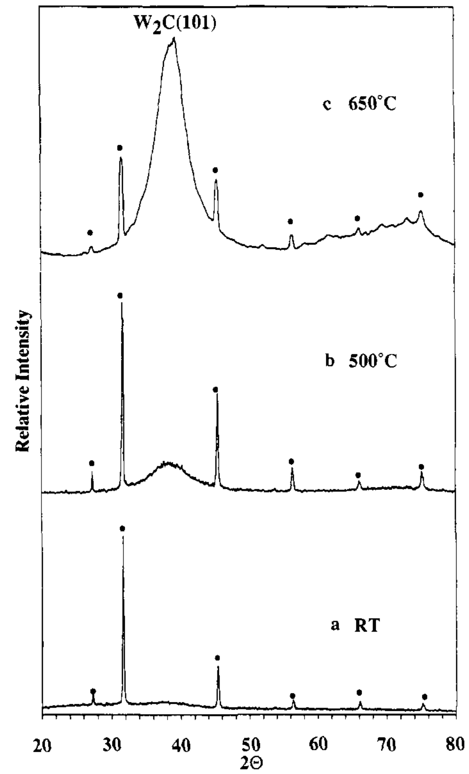

Figure 4. X-ray powder diffraction data obtained from the powder isolated from the reduction of WCl_4 in THF (a) and after heating to 500 (b) and 650 °C (c) for 4 h each, *in vacuo*. The peaks labeled ● correspond to NaCl, the remaining peaks correspond to W_2C.

identical before (Figure 5a) and after (Figure 5b) washing, as shown by SEM. Elemental analysis showed a slightly lower carbon content after the sample was washed with water which may due to a small amount of oxidation of W_2C. TGA of the water washed sample showed the conversion of W_2C to WO_2 based on a comparison of the calculated (14%) and observed (11%) weight gain by oxidation in air, consistent with the presence of W_2C rather than W or a tungsten oxide after water treatment.

(3) Synthesis of Metal Carbides by $LiBEt_3H$ Reduction of MCl_n in THF. The reduction of the chromium, molybdenum, and tungsten halides with either $NaBEt_3H$ or $LiBEt_3H$ in THF as solvent resulted in the formation of the corresponding metal carbides, M_2C, rather than the metals. The metal carbides were characterized by a variety of techniques including elemental analysis, X-ray powder diffraction, and electron microscopy. Analytical data revealed the presence of carbon in the crude samples prepared by reduction at room temperature.

The reduction of THF suspensions of $CrCl_3$ at room temperature with a slight excess of the stoichiometric amount of $LiBEt_3H$ resulted in the formation of a white solid at first, consistent with the reduction of $CrCl_3$ to $CrCl_2$. On continued addition of $LiBEt_3H$, $CrCl_2$ was further reduced to form a black suspension. Gas evolution, probably H_2, was observed throughout this reaction. After stirring for 24 h at room temperature, a homogeneous colloidal black solution was formed from which a black powder was separated. The unreacted $LiBEt_3H$ was destroyed by reaction with methanol. Combustion elemental analysis of this sample showed a lower carbon content than expected for Cr_2C, and some contamination with hydrogen and nitrogen. This may be caused by the extremely pyrophoric nature and air sensitivity of the as-prepared Cr_2C particles, even relative to the other carbides formed by this method. The product was identified as the phase Cr_2C by several analytical methods. X-ray powder diffraction showed that heat treatment at 450 °C for 3 h resulted in a broad diffraction peak centered at a *d* spacing of 2.1 Å consistent with the presence of Cr_2C (101) rather than Cr metal. When the sample was heated at 500 °C for 3 h, the X-ray powder diffraction pattern (Figure 6) showed that the peaks sharpened and were consistent with the presence of the crystalline phase Cr_2C. X-ray diffraction peaks at d-spacings corresponding to Cr_2O_3 (Figure 6) were also observed, probably due to the extreme oxidation sensitivity of this sample. SEM data revealed that the grain size of the black powder obtained at room temperature was approximately 200–300 nm and that the grains grew little on heating to 500 °C, even though the crystallite size changed extensively as determined by X-ray powder diffraction. TEM (Figure 7a) also showed the grain size of the as-prepared material was similar to that observed by SEM. However, TEM revealed that these grains were composed of agglomerates of smaller, approximately 5-nm-sized crystallites (Figure 7b). On heating to 500 °C, TEM revealed that the crystallites grew to a size of approximately 200–400 nm (Figure 8). Electron diffraction data were also consistent with this interpretation. The as-prepared material exhibited diffuse rings consistent with *d* spacings of Cr_2C, but the annealed material showed evidence for the presence of larger crystallites. Energy dispersive spectroscopy from both SEM and TEM showed that the as-prepared and heat-treated black powder exhibited peaks only attributed to chromium. No chlorine was detected within the detection limits of the instrument, and the lithium chloride byproduct was thought to have been removed in the washing steps, in contrast to sodium chloride above. Attempts to obtain the thermogravimetric analysis of the as-prepared sample failed due to the extremely pyrophoric nature of this material.

Reduction of $MoCl_4(THF)_2$ or $MoCl_3(THF)_3$ in THF at room temperature with a slight excess of stoichiometric amount of $LiBEt_3H$ resulted in the formation of a black colloid accompanied by hydrogen gas evolution. The reaction mixture turned to black immediately on addition of $LiBEt_3H$ in contrast to the $CrCl_3$ system. After stirring overnight at room temperature, a black colloid was formed that has previously been shown to be comprised of 2–4-nm-sized Mo_2C crystallites.[23] A black solid was separated from the colloidal solution by centrifugation. The black solid was washed with THF and methanol to ensure removal of any unreacted $LiBEt_3H$. Energy-dispersive spectroscopy from both SEM and TEM showed that the black powder contained molybdenum and no evidence for chlorine was observed. Both SEM and TEM showed that the grain size of the black powder was ~1–2 μm. TEM further revealed that these particles were agglomerates of 2-nm-sized primary particles. X-ray powder diffraction of the room-temperature product showed a broad diffraction peak centered at a *d* spacing of approximately 2.4 Å. Line broadening analysis of this XRD pattern was consistent with a crystallite size of 2 nm for the as prepared Mo_2C which was consistent with the TEM data. To confirm the characterization as Mo_2C, the sample was sintered at a number of different temperatures, *in vacuo*, to increase the crystallite size. On heating to 500 °C, the

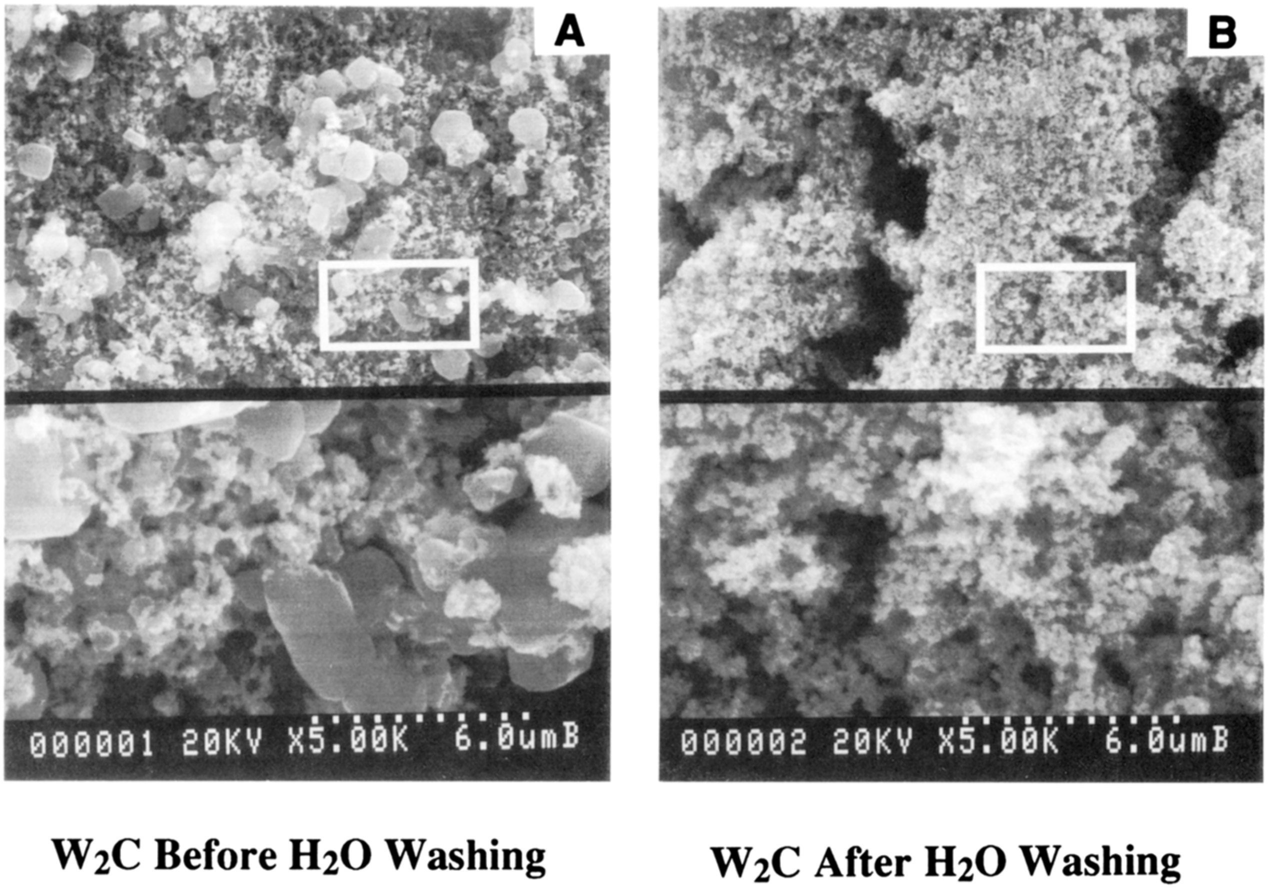

Figure 5. SEM micrographs showing that the morphology of the as-prepared W_2C powder (a) is not changed on washing (b) with deoxygenated water. The larger particles are NaCl.

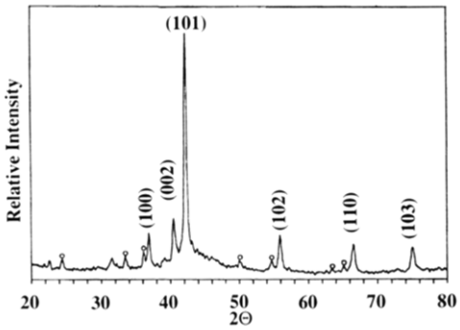

Figure 6. X-ray powder diffraction data obtained for the powder isolated from the reduction of $CrCl_3$ in THF after heating to 500 °C for 3 h, *in vacuo*. The peaks labeled ○ correspond to Cr_2O_3, the remaining peaks correspond to Cr_2C.

X-ray diffraction pattern (Figure 9) sharpened and corresponded to that of Mo_2C. No evidence for Mo was observed. To further confirm the existence of the carbon, combustion elemental analysis showed that the black powder contained 6.3% carbon, close to the calculated carbon percentage, 5.9% for Mo_2C. Thermogravimetric analysis of Mo_2C prepared at room temperature under air showed oxidation to form MoO_2 with an observed weight gain percentage of 25%, close to the calculated value (26%) expected for the conversion of Mo_2C to MoO_2.

When WCl_4 was reduced in THF at room temperature with a slight excess of the stoichiometric amount of $LiBEt_3H$, a black powder, W_2C, was isolated in high yield, 95% based on WCl_4. Both SEM and TEM data revealed that the grain size of the black powder was approximately 2–4 μm and were composed of agglomerated 1-nm-sized primary particles by TEM. The X-ray powder diffraction of the room temperature product showed that there was one broad diffraction peak centered at a *d* spacing of 2.3 Å. The broadening of the X-ray diffraction peaks corresponded to 1-nm-size crystallites which was consistent with the TEM data. After the sample was heated to 450 °C under vacuum, the X-ray diffraction pattern showed only peaks corresponding to W_2C. Elemental analysis confirmed the presence of the carbon in the sample. Thermogravimetric analysis under air resulted in oxidation of the W_2C to form the brown powder, WO_2 according to a 12% weight gain.

The issue of whether the carbon is present as a crystalline, stoichiometric metal carbide phase or as amorphous carbon in the as-prepared metal carbides is less clear. The diffraction maxima of the broad X-ray diffraction peak in all three phases corresponded more closely to the position expected for the crystalline carbide phase rather than the metal. If the metal and amorphous carbon were present rather than a single-phase metal carbide, it might be expected that either no crystalline phases would be present, or that the metal would be crystalline. In these cases, there would either be a broad peak characteristic of an amorphous sample[26] or diffraction peaks characteristic of the metal. However, on the basis of the X-ray and electron diffraction data, it appears that the peaks present are attributable to the diffraction maxima for the metal carbide phase. Infrared spectroscopy of a sample of crude Cr_2C revealed very low intensity peaks at 2930 and 2854 cm^{-1}, consistent with a small contamination with hydrocarbon or at least C–H bonds. Similar FTIR data were obtained for the Cr powder produced via reduction of $CrCl_3$ with $NaBEt_3H$ in toluene. These hydrocarbon peaks were present in the material

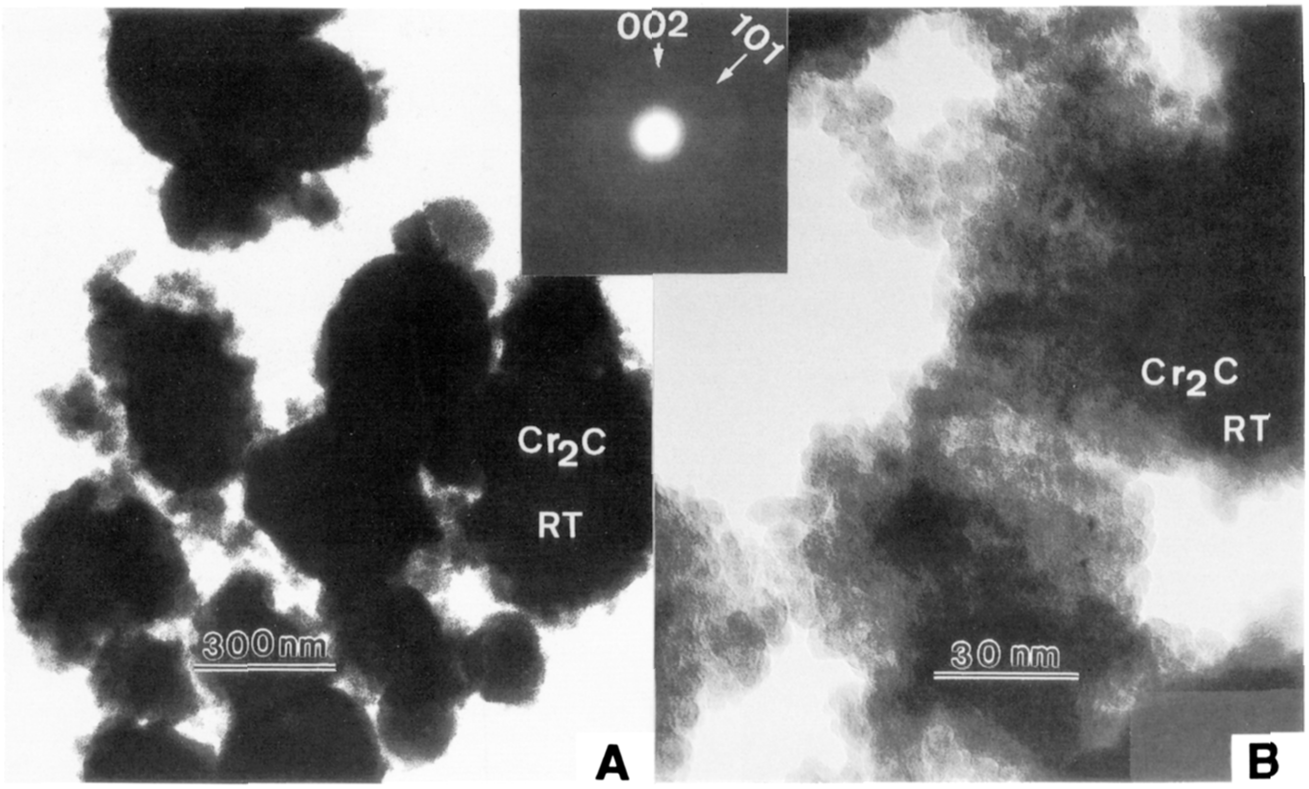

Figure 7. TEM micrographs and electron diffraction data for the as-prepared Cr_2C powder at two different magnifications, (a) and (b) emphasizing the agglomerate size and the primary particle (crystallite) size.

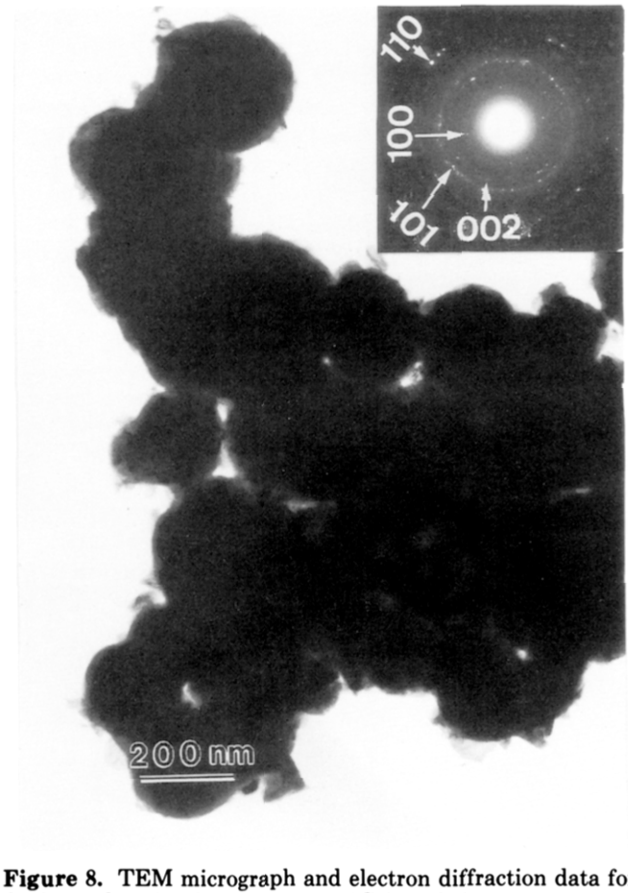

Figure 8. TEM micrograph and electron diffraction data for Cr_2C powder after heating to 500 °C for 4 h *in vacuo.*

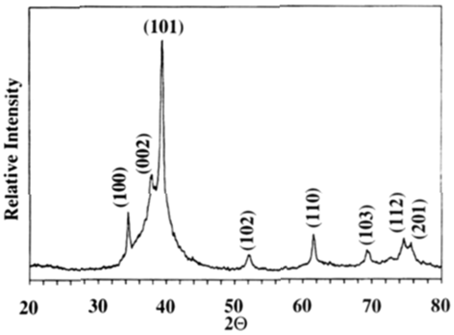

Figure 9. X-ray powder diffraction data obtained from the powder isolated from the reduction of $MoCl_3(THF)_3$ in THF after heating to 500 °C for 4 h in vacuo.

that was reduced using either toluene or THF as a solvent. Another possibility is that these peaks arise from the presence of BEt_3 coordinated to the surface of the particles. However, when these materials were digested in concentrated nitric acid, no evidence for boron was observed by atomic absorption spectroscopy. Furthermore, no differences were observed in the metal carbide samples as a determined by *ex situ* variable temperature X-ray diffraction, *with* or *without* methanol washing steps. This indicates that the carbon originated from the initial reduction reaction. It is possible that further information to determine whether a crystalline phase has been formed initially may be derived from catalytic hydrogenation experiments.

The origin of the carbide is still uncertain at this stage. Initially, we proposed that the formation of the carbide may have been due to transfer of an ethyl anion rather than hydride from the triethylborohydride reducing reagent to the metal center. Ethyl groups normally rearrange to liberate the ethylene and result in formation of a metal hydride.[29] Therefore, it seems more likely that the common factor in the formation of the *metal carbide* rather than the *metal* is the solvent and not the reagents.

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[29] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In Principles and Applications of Organotransition Metal Chemistry; University Science Books: Berkeley, CA, 1987.

The metal carbides are only formed when the reduction is carried out in the presence of THF as solvent. We had initially ruled out this possibility because we expected that reaction of the metal with THF might be more likely to result in formation of a metal-oxygen bond rather than a metal–carbon bond. However, it has recently been demonstrated that the reaction of a reduced molybdenum species with THF as solvent resulted in formation of a metal carbon bond according to the reaction of eq 3.[30] The

$$[(\eta^5\text{-}C_5H_5)_2MoSnPh_3]^- + Me_3SiCl \xrightarrow{THF} [(\eta^5\text{-}C_5H_5)_2(Ph_3Sn)Mo(CH_2)_4OSiMe_3] + Cl^- \quad (3)$$

outcome of this reaction appears to be strongly influenced by the oxophilicity of the silicon reagent because reaction of the same anionic molybdenum complex with Me_3SnI or CH_3I in THF resulted in formation of the normal substitution product, e.g., $[(\eta^5\text{-}C_5H_5)_2(Ph_3Sn)MoSnMe_3]$. In the case of the reactions to form the metal carbides, it would seem that if a metal carbon bond is formed in a intermediate step, it might be expected that subsequent β-hydride elimination would result in formation of a metal hydride bond with elimination of the carbon containing fragment as an olefin.[29] Hydrogen abstraction from a metal-bonded carbon would lead to retention and strengthening of the metal carbon bond.

In order to investigate the role of THF and $LiBEt_3H$ in the reduction reactions further, WCl_4 was reduced with $NaBEt_3H$ in toluene solution to form nanocrystalline W. The W powder, together with NaCl as a byproduct, was isolated by centrifugation as described above. The powder was annealed at 500 °C for 4 h and X-ray powder diffraction data revealed the presence of nanocrystalline W together with crystalline NaCl as shown in Figure 10a. A portion of this black powder was stirred in THF for 24 h and formed a colloid. Half of this colloid was then centrifuged and a powder was isolated and annealed at 500 °C for 4 h. The X-ray powder diffraction pattern of the annealed materials revealed the presence of nanocrystalline W (see Figure 10b). To the other half of the THF colloid, $LiBEt_3H$ was added and the mixture stirred for 24 hr. The X-ray powder diffraction pattern obtained from the isolated black powder after annealing at 500 °C for 4 h also revealed the presence of nanocrystalline W (Figure 10c). No evidence for the formation of W_2C was observed in these reactions. The X-ray powder diffraction pattern for W_2C obtained from the $NaBEt_3H$ reduction of WCl_4 in THF is presented in Figure 10d for comparison. While these experiments do not reveal the origin of the C in M_2C, it is clear that the carbide must be formed at an early stage during the reduction reaction and not subsequent to the formation of the metal.

The oxidation behavior of these materials has not been fully addressed in this work. It is quite possible that the metals and metal carbides possess a surface oxide layer, especially since exposure to the atmosphere could not be avoided during collection of much of the characterization data. In the case of chromium, the formation of crystalline oxide was observed on heating Cr_2C. However, for the other metal and metal carbide phases prepared here, X-ray diffraction data did not reveal the presence of crystalline oxide or oxycarbide phases. Therefore, we propose that while the surface of these particles may be oxidized, the bulk of the material must be unoxidized to be consistent with the characterization data obtained. Indeed, surface oxidation may passivate the particles toward further oxidation. Intentional oxidation, caused by heating the particles in air resulted in the weight gains described above in the TGA experiments and formation of crystalline oxide phases. It seems likely that bulk oxidation occurs in these cases. In separate experiments, the thermal oxidation of W in air at 800 °C for 30 min resulted in formation of crystalline WO_3. An alternative explanation to oxidative passivation of the surface is that the liberated BEt_3 coordinates to the surface and provides temporary passivation. On thermally induced crystallite growth, the weakly coordinated, volatile BEt_3 could molecularly desorb and result in formation of oxide free materials. The absence of a surface oxide passivation layer is consistent with the observation that the reaction of the M_2C powders prepared in this work with elemental Si powder results in the formation of the corresponding metal silicide and silicon carbide where no evidence for the formation of metal oxides was observed.[38]

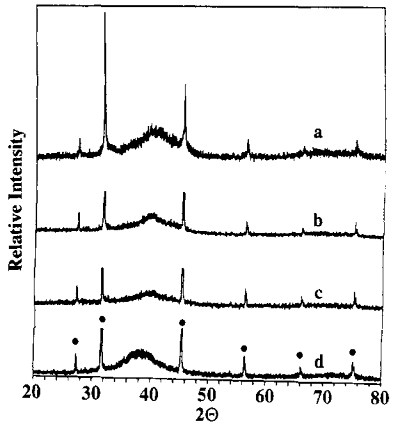

Figure 10. X-ray powder diffraction data for product of reduction of WCl_4 with $NaBEt_3H$ in toluene: (a) after annealing at 500 °C for 4 h, (b) after suspension in THF at room temperature for 24 h and annealing at 500 °C for 4 h and (c) after suspension in THF and $LiBEt_3H$ at room temperature for 24 h and annealing at 500 °C for 4 h. The X-ray diffraction pattern shown in (d) is that of nanocrystalline W_2C derived from the reduction of WCl_4 with $NaBEt_3H$ in THF. The peaks labeled ● correspond to NaCl.

Conclusions

In summary, these experiments have shown that reduction of group 6 metal chlorides in toluene by sodium triethylborohydride results in formation of the corresponding metal, whereas reduction by either lithium or sodium triethylborohydride in THF results in formation of the corresponding metal carbide, M_2C phase as shown in Scheme I. Colloids are formed initially from which black powders can be isolated by centrifuging the solution.

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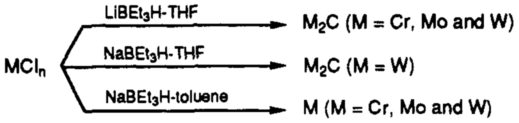
Scheme I[a]



[a] M = Cr or Mo, n = 3; M = W, n = 4.

TEM and electron diffraction data of the colloids deposited on copper-coated grids show that 1–5-nm-sized crystallites were formed. The metal and metal carbide powders derived from the colloids by centrifuging and washing with various solvents were characterized with SEM, TEM, EDS, and ED and showed that the powders were comprised of agglomerates of the primary crystallites. X-ray powder diffraction studies of these black powders exhibited broad peaks for the as-prepared powders at room temperature where the broadening generally corresponded to the primary crystallite size as determined by TEM. Variable-temperature X-ray powder diffraction allowed unambiguous identification of the crystalline metal and metal carbide phases present. Carbon and hydrogen combustion elemental analysis was also used to identify the metal and metal carbide materials. Thermogravimetric analysis in air provided information on the oxidation behavior of the materials and also enabled some distinction between the formation of metals versus metal carbides, M_2C.

Existing routes to these interstitial carbide materials, M_2C, generally involve either high temperature (>1200 °C) reduction of the corresponding metal oxide[31–34] or halide[35] or ball-milling mixtures of elemental powders for extended periods at lower temperatures.[36,37] Both these methods often result in additional reactions between the reagent and container causing contamination with impurities. The synthetic procedures described here may be valuable for the preparation of nanophase metals and metal carbides for subsequent low-temperature reactions. The reaction of the metal carbides with silicon to form metal silicides and silicon carbide under relatively mild conditions as a result of the small primary particle size will be reported elsewhere.[38]

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