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Room Temperature Synthesis of Crystalline Molybdenum and Tungsten Carbides, Mo_2C and W_2C, via Chemical Reduction Methods

by

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Room Temperature Synthesis of Crystalline Molybdenum and Tungsten Carbides, Mo_2C and W_2C, via Chemical Reduction Methods.

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Abstract:

The species $MoCl_3(THF)_3$, $MoCl_4(THF)_2$ and WCl_4 have been reduced in THF solution with $LiBEt_3H$ to give black, homogeneous solutions. The black product could be separated from the other reaction by-products to give either a colloidal black solution or an agglomerated black precipitate. TEM of the dried colloidal solutions showed the presence of monodispersed 1-2nm sized particles which gave a broad electron diffraction rings corresponding to a d-spacing of ~2.4Å. Energy dispersive spectroscopy showed only the presence of Mo or W depending on which starting material was used. The black precipitates were shown to be agglomerates of the 1-2nm crystallites. X-ray powder diffraction data also showed a broad peak centered at 2.4 Å for Mo_2C and 2.3Å for W_2C. On heating the peaks sharpened and a number of other lower intensity peaks emerged that were consistent with the presence of crystalline M_2C (M = Mo, 500°C or W, 450°C) rather than the expected metal products. The identity of M_2C was confirmed by elemental analysis and by TGA oxidation experiments.

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998 words and 2 Figures

The preparation of nanometer-sized particles of phase pure materials is currently attracting intense interest in materials chemistry because such particles exhibit unique chemical and physical properties that are intermediate between those of molecules and extended solids.[1] For example, metal chalcogenides exhibit size dependant physical properties in the 2-100 nm size regeme[2] and metal particles exhibit size-dependant selectivity[3] and reactivity[3,4] in catalytic reactions. However, traditional solid-state synthetic methods seldom result in formation of particles smaller that 100nm.[5] New synthetic routes based on chemical methods show promise for the formation of materials with a homogeneity, morphology, composition, microstructure and purity not otherwise obtainable. For example, the reduction of metal salts in the presence of a surfactant, often in inverse micelles, has led to formation of mono-dispersed nanometer-sized particles.[6] However, the surfactant can lead to impurity incorporation in subsequent steps and as a result a number of groups are investigating alternative synthetic strategies. Reicke et al.[7] have extensively investigated the reduction of metal salts with alkali metal naphthalenides and formed highly dispersed, reactive metal powders. Bonnemann et al.[8,9] have shown that trialkylborohydride reducing agents can be used to reduce a variety of metal complexes to form the corresponding metal colloids. The metals are reasonably pure (70% - 98%), the particle size was approximately 10-100nm and generally crystalline materials were formed depending on the specific system as determined by X-ray diffraction.

Here we report the room temperature reduction of molybdenum and tungsten halides with LiBEt$_3$H, which results in the formation of monodispersed, 1 and 2nm, crystalline Mo$_2$C and W$_2$C colloids, respectively, rather than formation of the metal. Existing routes to these interstitial carbide materials involve either high temperature (> 1200°C) reduction of the corresponding metal oxide[10-13] or halide[14] or ball-milling mixtures of elemental powders for extended periods at lower temperatures.[15, 16] Both these methods often result in addition reactions between the reagent and container causing impurity incorporation.

The reduction of THF suspensions of MoCl$_4$(thf)$_2$, MoCl$_3$(thf)$_3$ and WCl$_4$ at -10°C with a slight excess of the stoichiometric amount of LiBEt$_3$H resulted in the formation of a black solution accompanied by gas evolution.[17] After stirring for 24hr., the colloidal solutions generally aggregated and black powders could be isolated by centrifugation. Under some conditions, the black powders could be isolated and redispersed in THF to give black colloidal solutions. For $MoCl_3(THF)_3$, a representative example, the black powder isolated had a particle size of approximately 1-2µm (SEM) and contained only Mo by energy dispersive spectroscopy. Closer examination by transmission electron microscopy revealed that the 1-2µm sized particles were agglomerates of smaller, 2nm sized particles. Energy dispersive spectroscopy revealed only Mo and electron diffraction revealed a diffuse ring at a d-spacing corresponding to ~2.4Å, consistent with the very broad peak observed for the same sample by X-ray powder diffraction. TEM of a sample of the same material redispersed in THF revealed the presence of monodispersed particles approximately 2nm in diameter, Figure 1. This particle size is consistent with the broadening observed by X-ray diffraction as calculated from the Scherrer equation and so also represents the crystallite size. Due to the broadness of the X-ray diffraction peak and the similarity between the crystal structures of Mo and Mo_2C a distinction between these species could not be made at this stage. To distinguish these two possibilities, the sample was sintered at a number of different temperatures, *in vacuo*, to increase the size of the crystallites. On heating to 500°C, the X-ray diffraction pattern sharpened and corresponded to that of Mo_2C. No evidence for Mo was observed. The X-ray diffraction data for W_2C as-prepared at room temperature and after heating to 450°C *in vacuo* are presented in Figure 2. Higher temperature sintering of Mo_2C at 10^{-2} torr resulted in partial oxidation to form traces of crystalline Mo, MoO_2, as determined by X-ray diffraction, and presumably CO_2. Thermogravimetric analysis in air quantitatively confirmed this oxidation to MoO_2 via an observed weight gain of 25% (calculated, 26%).

Similar observations were made for the formation of Mo_2C from $MoCl_4(thf)_2$ and W_2C from WCl_4. The interstitial carbides were formed in high yields (>93%) and were all composed of 1-2 nm sized primary crystallites which sintered to enable unambiguous phase assignment at 450 - 500°C. The presence of carbon in all as-prepared samples prior to sintering was confirmed by combustion elemental analysis. The origin of the carbide has not been identified at this stage. However, evidence that it is incorporated in the initial reaction rather than in a subsequent washing and isolation step comes from a separate experiment in which the crude, centrifuged, aggregated black powder formed from reduction of $MoCl_3(THF)_3$ was found to be Mo_2C by variable temperature X-ray powder diffraction. Presently, we feel that it is unlikely that the carbide originates from the solvent (THF) since decomposition of the solvent is more likely to lead to metal oxide formation, and we currently suspect that $LiBEt_3H$ is the source of carbide. Consistent with this proposal, the reduction of $MoCl_3(THF)_3$ with $LiBH_4$ under the identical reaction conditions to the $LiBEt_3H$ reduction reactions described above, did *not* result in formation of Mo_2C as determined by X-ray powder diffraction after heating the product to 500°C.

We have observed that a key feature to the success of these experiments is the purity of the starting materials. When $MoCl_3(THF)_3$ is prepared according to the literature method[18] which involves reduction of $MoCl_4(THF)_2$ with tin powder, we have found that after reduction and separation, tin was always incorporated in the final product as determined by energy dispersive spectroscopy. As part of these studies, we have recently reported[19] a single step method for the preparation of high purity $MoCl_3(THF)_3$ in high yield by the reduction of $MoCl_5$ with two equivalents of diphenylsilane. Further studies are in progress to unambiguously determine the origin of the carbide in these materials and to explore the generality of this reduction method.

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17. A representative example of the preparation of Mo_2C is presented here:

    Trichlorotris(tetrahydrofuran)molybdenum(III) (6.03 gram, 14.43 mmole) was suspended in 150 mL THF which was cooled by ice/NaCl/H_2O cooling bath. Into this suspension, 50.0 mL of 1.0M $LiBEt_3H$/THF was added slowly (in about 2 minutes) by using syringe. Immediate color change from red-brown to black accompanied by a gas evolution was observed. After 24 hours subsequent stirring at room temperature. The black suspension was centrifuged to give black solid which after washing with THF, EtOH and THF, was pumped to dry give 1.36 gram black powder Mo_2C, a yield of 93% based on $MoCl_3(thf)_3$. Elemental analysis. Calcd for Mo_2C: C, 5.88%, H, 0%. Found: C, 6.43%; H, 1.07%. From $MoCl_4(THF)_2$: elemental analysis. Calcd for Mo_2C: C, 5.88%, H, 0%. Found: C, 6.32%; H, 1.04%.

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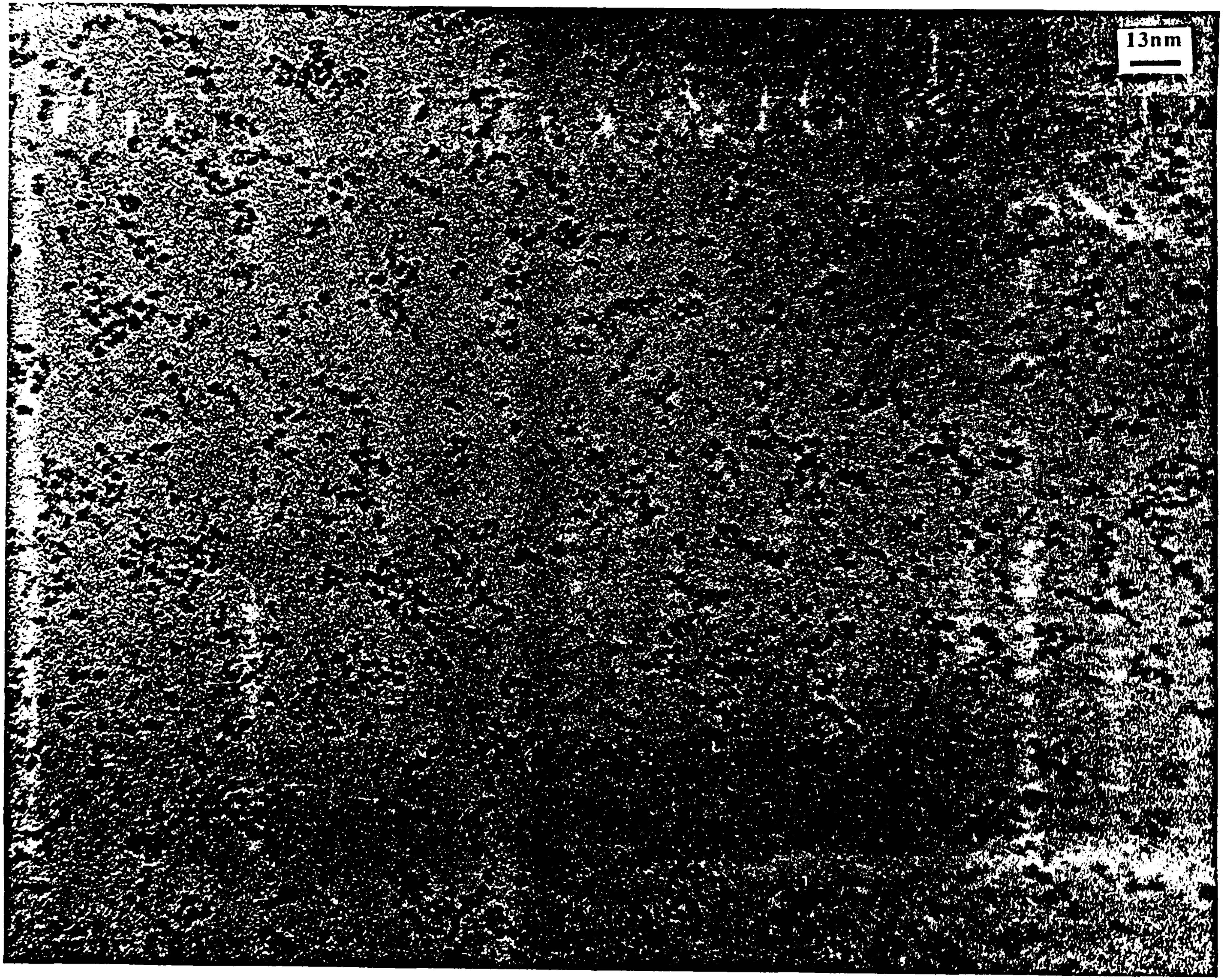
Figure Captions

Figure 1: TEM data for Mo_2C particles formed by reduction of $MoCl_3(THF)_3$ with $LiBEt_3H$ in THF.

Figure 2: Variable temperature X-ray powder diffraction data for W_2C showing the growth of the crystallites with increasing temperature and confirming the presence of crystalline W_2C. Lower pattern is the data obtained at room temperature. The upper pattern was obtained after heating to 450°C.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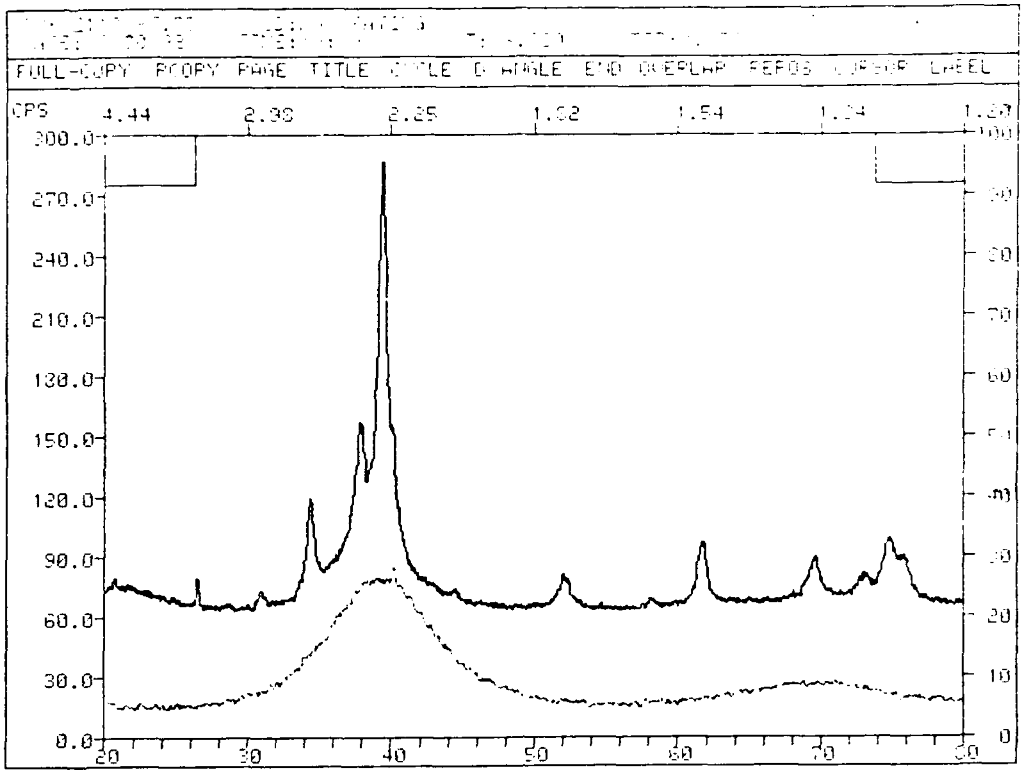
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