

行政院國家科學委員會專題研究計畫成果報告

分子化合物合成無機材料之新方法(二)

NEW MOLECULAR ROUTES

TO INORGANIC MATERIALS (2) -

**Preliminary Investigation of Nano-Sized Early Transition Metal Carbides
Synthesized from Metal Chlorides and n-Butyl Lithium**

計畫編號：NSC 87-2113-M-009-005

執行期限：86年8月1日至87年7月31日

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一、中文摘要

本計畫繼續本研究室之研究，以分子化合物為前驅物，合成無機材料。研究發現奈米金屬碳化物粉末，可以溶液相使用過渡金屬氯化物與丁基鋰中反應，再經熱處理合成。其中過渡金屬為鈦，鈳，鈳，鈳，鈳，鈳，鈳，鈳。丁基之 β -氫脫去反應可能扮演重要角色，分解為丁烷及丁烯。並提供金屬碳化物中碳原子之來源。

關鍵詞：金屬碳化物粉末，奈米材料，溶液相合成，低溫反應

Abstract

Ceramic materials with uniform elemental compositions can be synthesized employing molecular precursors via solution routes at low temperatures. Here, we report our exploratory syntheses of nano-sized early transition metal carbides using this strategy at temperatures significantly lower than the traditional methods.

In an air-free environment, metal halides of groups 4-6, TiCl_4 , VCl_3 , TaCl_5 and MoCl_5 were allowed to react with Bu^nLi in hexane to form n-butane, 1-butene, LiCl and black colloids. These air-sensitive

colloids, used as the precursors to carbides, were separated, dried under vacuum, and processed further. LiCl and other volatile byproducts were removed by vacuum sublimation at 923 K. After this step, the black powders, still air-sensitive, were shown to be amorphous by XRD. They were proposed to be nano-sized metal carbides. After annealed under vacuum at temperatures higher than T, the powders showed diffraction patterns, using XRD and/or ED, of the following metal carbides. These were TiC at $T > 1173$ K, V_4C_3 at $T > 1023$ K, TaC at $T > 973$ K, and Mo_2C (mixed with Mo) at $T > 1173$ K, from the reactions using TiCl_4 , VCl_3 , TaCl_5 and MoCl_5 , respectively. Their sizes were in the range of 20 - 100 nm, as shown by STEM and/or estimated using Scherrer equation.

Keywords: metal carbides, nano particles, solution synthesis, low temperature processing

Introduction

Early transition metal carbides have very interesting properties [1-2]. Generally, they are highly refractory and chemically inert and with many technology uses. However, unlike many other ceramic

materials such as oxides which can be produced from raw materials found in nature, the refractory carbides generally do not exist in the natural state. They have to be synthesized through costly high temperature processes. For example, reacting metal oxides with carbon in the presence of hydrogen at temperatures near 2300 K is one method frequently applied to prepare metal carbide powders. Here, we wish to report our exploratory syntheses of nano-sized early transition metal carbides with uniform elemental compositions at temperatures significantly lower than the traditional methods. The method employed reacting molecular precursors in solution to obtain colloids at low temperatures, followed by heat treatment under vacuum at temperatures above 873 K.

Results and Discussion

In an air-free environment, metal halides of groups 4-6, TiCl_4 , ZrCl_4 , VCl_3 , NbCl_5 , TaCl_5 , CrCl_3 , MoCl_5 and WCl_6 were allowed to react with Bu^nLi in hexane to form n-butane, 1-butene, LiCl and black colloids. These air-sensitive colloids, used as the precursors to carbides, were separated, dried under vacuum, and processed further.

LiCl and other volatile byproducts were removed by vacuum sublimation at 923 K. After this step, the black powders, still air-sensitive, were shown to be amorphous by XRD. They were proposed to be nano-sized metal carbides. After annealed under vacuum at high temperatures, the powders showed diffraction patterns of metal carbides, using XRD and/or ED. For example, the powders processed from TiCl_4 and Bu^nLi at $T > 1173$ K, showed very fine structures using STEM with the sizes under 20 nm. The XRD and ED patterns indicated that the powders are cubic phase titanium carbide, TiC . The powders processed from VCl_3 and Bu^nLi at $T > 1023$ K, showed very fine structures using STEM with the sizes under 20 nm. The XRD and ED patterns indicated that the powders are cubic phase vanadium carbide, V_4C_3 . The powders processed from TaCl_5 and Bu^nLi at $T > 973$ K, showed very fine structures using STEM with the sizes under 20 nm also. The XRD and ED patterns indicated that the powders are cubic phase tantalum carbide, TaC . The powders processed from MoCl_5 and Bu^nLi at $T > 1173$ K, showed fine structures using SEM. The XRD patterns indicated that the

powders are cubic phase molybdenum carbide Mo_2C mixed with Mo metal. Elemental analysis of the powders showed that the C concentration varied from sample to sample. Some metal carbides had elemental composition of the stoichiometric formula while others showed deficiency, indicating incomplete filling of the interstitial holes, or excess in carbon concentrations, a sign of graphite carbon presence. X-ray photoelectron spectroscopy would be a very useful tool to distinguish between graphite and carbide type of carbon atoms. Investigations are planned to be carried out in the near future. Volatile byproducts collected at liquid nitrogen temperature and NMR tube reactions indicated that butane and butene are the two major organic products generated in the process. This observation supports a β -hydrogen elimination initiated reduction of the metal centers, followed by polymerization of the metal fragments into colloids. Further heat-treatment of the colloids transformed residual hydrocarbon fragments bonded to the metal centers, probably in the form of coordinated alkenes, alkylidenes or alkylidynes, into carbidic carbons. Excess hydrocarbon fragments may

also polymerize into organic polymers and then pyrolyzed into graphite carbons.

In conclusion, this research has shown that by proper selection of reaction precursors, transition metal carbides can be prepared at temperatures significantly lower than the ones employed in the traditional methods. The origin of this improvement is probably due to the formation of metal-carbon bonds at low temperatures in solutions. These bonding interactions caused uniform mixing of the elements at atomic levels and lowered subsequent processing energy barriers for metal carbide formation. We found the process is a general route to early transition metal carbides. We speculate that using other alkyllithium reagents will provide similar results. We will proceed in this new area rich in fundamental chemistry and technologically important area for further exploration.

References

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