



Thermal analysis and vapour pressure of a new series of tungsten(VI) oxo-alkoxide- β -ketoesterate complex precursors for the chemical vapour deposition of tungsten oxide

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ARTICLE INFO

Article history:

Received 12 February 2008

Received in revised form 11 April 2008

Accepted 28 April 2008

Available online 3 May 2008

Keywords:

Tungsten oxide

Chemical vapour deposition

β -Ketoesterate complexes

Thermogravimetry

Vapour pressure

Langmuir equation

ABSTRACT

A new series of tungsten complexes, tungsten(VI) oxo-alkoxide- β -ketoesterate complexes have been synthesized and characterized by infrared and NMR spectroscopy. Thermogravimetric analysis has been carried out on the complexes as a function of temperature, and isothermally as a function of time. Based on the thermal analysis data, these complexes are evaluated for their suitability as precursors for the chemical vapour deposition of tungsten oxide thin films. The vapour pressure of these precursors is estimated using the Langmuir equation.

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1. Introduction

Tungsten oxides have been studied extensively because of their possible applications in electrochromic devices [1] and gas sensors [2]. Thin films of tungsten oxide have been prepared for these applications by various physical and chemical methods of film deposition, often leading to different properties [1]. In particular, tungsten oxide thin films have been prepared by a range of chemical vapour deposition (CVD) techniques. CVD is an important method of preparation of thin films as it has advantages such as conformal coverage, high purity of films, low temperature processing and economy of large scale coatings. WO_3 films have been grown by low-pressure CVD using tungsten hexacarbonyl ($W(CO)_6$) as precursor [3] which is highly toxic and also using tungsten alkoxides as precursor [4]. Other precursors such as tungsten oxychloride ($WOCl_4$) [5] and tungsten hexafluoride (WF_6) [6] have also been used for CVD of tungsten oxide. However, these precursors have problems such as high reactivity, corrosivity and difficulty in handling.

In 1996, the use of volatile tungsten(VI) oxo alkoxide- β diketone complexes of the type $[WO(OR)_3L]$ (R = isopropyl (iPr),

$tert$ -butyl (tBu); L = acetyl acetonate (acac), hexafluoro acetyl acetonate (hfac)) as precursors for the metal organic CVD (MOCVD) of tungsten oxide was reported [7]. However, the thermal analysis of these compounds was not reported therein, nor later in the literature. Thermal analysis of precursors is very important for their application to CVD. Furthermore, the use of fluorinated precursors for CVD has many disadvantages, due to the high toxicity and corrosivity of the fluorine. It is thus desirable to develop halogen-free precursors for CVD, and to examine their volatility through thermal analysis.

Here we report the synthesis, characterization and thermal analysis of a related series of compounds, tungsten(VI) oxo alkoxide β -ketoesterate complexes of the type $[WO(OR)_3L]$ with R = isopropyl, $tert$ -butyl; L = methyl acetoacetate (meob), ethyl acetoacetate (etob). Thermal analysis as a function of time and temperature allow us to suggest the suitability of these precursors for MOCVD applications. Further, from the differential thermogravimetry data, the vapour pressure of the precursors has been calculated with the Langmuir equation, using a recently reported procedure [8].

2. Experimental

The four complexes prepared and studied are $[WO(O^tBu)_3acac]$ I, $[WO(O^iPr)_3acac]$ II, $[WO(O^tBu)_3meob]$ III and $[WO(O^tBu)_3etob]$

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IV, and will be referred to henceforth by their corresponding roman numerals. The complexes were prepared by a method reported earlier for the complexes I and II ([7] and references therein), starting from tungsten oxychloride (WOCl_4), which was prepared by reacting WO_3 with SOCl_2 in a sealed tube at 200°C [9]. The WOCl_4 so obtained was dissolved in dry tetrahydrofuran (THF), and reacted with 4 equivalents of potassium *tert*-butoxide at 0°C to form the alkoxide complex $[\text{WO}(\text{O}^t\text{Bu})_4]$ and precipitating KCl [10]. To this complex 1 equivalent of β -ketoesterate ligand was added, and the mixture warmed and stirred for 5 h. The mixture was then filtered and solvent removed under vacuum to give the final product $[\text{WO}(\text{OR})_3\text{L}]$.

The complexes so prepared were characterized by infrared (IR) spectroscopy on a JASCO 410 FT-IR spectrometer. NMR spectroscopy was carried out on a Bruker AMX 400 400 MHz spectrometer. C_6D_6 was used as solvent and TMS was used as reference. Mass spectra of the compounds were recorded on a Micromass ESI-TOF mass spectrometer

Thermogravimetric/differential thermal analysis was carried out on the compounds, both as a function of temperature, and isothermally as a function of time at different temperatures, to examine their suitability as precursors for chemical vapour deposition. The thermal analysis was carried out on a TA Instruments SDT Q600 simultaneous DSC/TGA analyzer. All the TG experiments were carried out in flowing dry nitrogen, with a heating rate of $10^\circ\text{C}/\text{min}$. About 15 mg of the compound was used for the analysis, with alumina as the reference material. Isothermal experiments were carried out by ramping the temperature at $10^\circ\text{C}/\text{min}$ to the isothermal temperature, then allowing the system to stay at that temperature for 15 min.

The Langmuir equation [8] was used to calculate the vapour pressure of the precursors.

$$P = \left[\left(\frac{dm}{dt} \right) \sqrt{\frac{T}{M}} \right] \left[\frac{\sqrt{2\pi R}}{\alpha_1} \right] \quad (1)$$

where P is the vapour pressure at temperature T , dm/dt is the rate of weight loss per unit surface area during the TG experiment, M is the molecular mass of the material, R is the gas constant, and

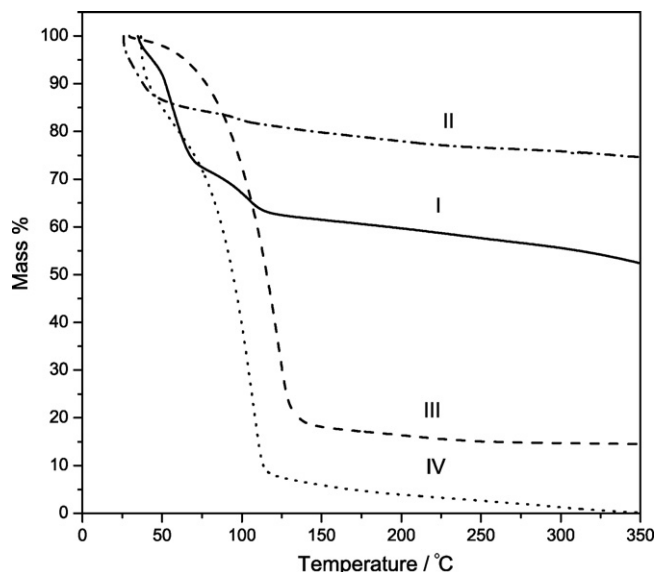


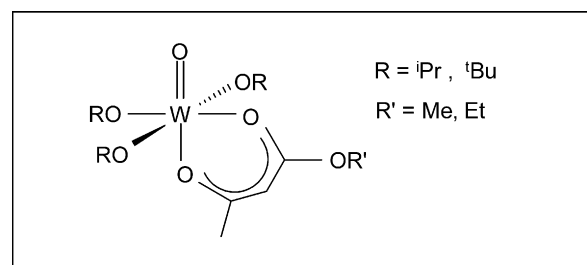
Fig. 1. TGA plot for the complexes I $[\text{WO}(\text{O}^t\text{Bu})_3\text{acac}]$, II $[\text{WO}(\text{O}^i\text{Pr})_3\text{acac}]$, III $[\text{WO}(\text{O}^t\text{Bu})_3\text{meob}]$ and IV $[\text{WO}(\text{O}^t\text{Bu})_3\text{etob}]$.

α_1 is the vapourization coefficient. In vacuum, α_1 is assumed equal to 1, but in the flowing gas environment of the TG experiment, α_1 is significantly different, and has to be determined experimentally. The term $[\sqrt{2\pi R}/\alpha_1]$ is often referred as k in the literature. Benzoic acid was used as a standard to determine ' k '. The vapour pressure for benzoic acid was taken from literature [11]. Using this value of ' k ', the vapour pressure was calculated for the compounds III and IV. The Clausius–Clapeyron equation, plotted as $\ln P$ vs. $1/T$ gives a straight line, the slope of which is $\Delta H/R$, was used to obtain the enthalpy of sublimation.

The vapour pressures of complexes III and IV have been calculated using the Langmuir equation. To do so, the value of ' k ' was first determined to be $90,606 \text{ kg}^{1/2} \text{ m s}^{-1} \text{ K}^{-1/2}$, using benzoic acid as the standard [8]. Employing this value of k , vapour pressure was calculated as a function of temperature for the complexes III and IV.

3. Results and discussion

The molecular structure of the complexes is shown below



The various complexes I–IV were characterized by infrared (IR) spectroscopy. The IR spectra of the complexes showed all the bands corresponding to the expected IR bands for the molecules. The IR bands for $\text{C}=\text{O}$ and $\text{C}=\text{C}$ of the ketoesterate ligand are observed at 1568 and 1531 cm^{-1} respectively. The band for the $\text{C}-\text{O}$ and $\text{C}-\text{H}$ are seen at 1280 and 2940 cm^{-1} respectively. The tungsten–oxygen bonds are observed around 450 and 670 cm^{-1} , confirming the formation of the complex.

The NMR spectra of the compounds I and II have been reported earlier [7]. In this work, the ^1H and ^{13}C NMR spectra of the complexes III and IV were recorded using C_6D_6 as solvent. The NMR data are consistent with that reported earlier for I and II [7]. The NMR data indicates the structure of the complexes to be of the type presented above. The doublet peak observed at $\delta = 31.3 \text{ ppm}$ in the ^{13}C spectrum corresponding to CH of the meob ligand indicate the structure to be as shown above. This is further supported by the presence of the singlet peak at $\delta = 5.0 \text{ ppm}$ in the ^1H NMR spectrum. All the other peaks in the ^1H and ^{13}C NMR spectra can be assigned to the same structure.

The mass spectra of the compounds show all the expected fragments. Thus, the formation of these compounds is confirmed by IR, NMR and mass spectroscopy. Mass spectroscopy did not show the molecular ion peak, as the complex fragments in the high energy electron beam, but the fragments observed confirm the validity of the structure.

The weight loss of the complexes was studied as a function of temperature. The graph showing the thermograms of the complexes I–IV is given in Fig. 1. It is observed that, in the case of the β -diketonate complexes, the volatility is high even at relatively low temperatures. However, the volatility of the β -ketoesterate complexes is even higher, with weight loss of the order of 80–90% occurring in the temperature range 50 – 150°C . It is also observed

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