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## A thermal analysis study of tungsten oxide gels

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### Abstract

A simultaneous TG–DTA–MS study was made in a helium flow for an amorphous gel prepared by the addition of water to an ethanolic solution of tungsten hexachloride before evaporating the solvent at ambient temperature. Four endothermic mass losses were observed at approx. 40–80, 130–170, 190–200 and 210–600°C. The first was attributed to desorption of hydrochloric acid and water. The second was attributed to the simultaneous evolution of (1) hydrogen chloride and ethylene, and (2) chloroethane. The third occurred very rapidly and was attributed to the same gases as the second loss. The fourth occurred very slowly and was attributed to the desorption of hydrogen chloride. The firing process of the gel was discussed on the basis of the decomposition mechanisms.

*Keywords:* DTA; MS; Sol-gel; TG; Tungsten oxide

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### 1. Introduction

One of the present authors reviewed [1] and investigated the formation process of ceramic films by thermal analysis of the precursor materials, for example, indium (III) 2-ethylhexanoate, calcium hydroxide and tin (II) iodide, forming the films of  $\text{In}_2\text{O}_3$  [2],  $\text{CaO}$  [3] and  $\text{SnO}_2$  [4], respectively. As part of this scheme, the formation process of tungsten oxide prepared by the sol-gel process was investigated in the present work.

Tungsten oxide films are of considerable interest for applications as the active layers of electrochromic window devices [5, 6]. The structure and properties of tungsten oxide prepared by sol-gel processes have been discussed in connection with the firing process [7–10].

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However, there is no experimental report discussing the gas species evolved from the tungsten oxide gels. The purpose of the present paper is to investigate the firing process of a gel prepared from tungsten hexachloride, and, in particular, to determine the gas species evolved from the gel decomposed in a helium atmosphere by TG–DTA–MS.

## 2. Experimental

### 2.1. Gel preparation

The preparation of the gel was carried out under an argon atmosphere. Tungsten hexachloride (1 g) was dissolved at ambient temperature in ethanol (10 ml), which was dried using molecular sieves and degassed by bubbling argon before use. The color of the solution turned blue when dissolved, which indicated the existence of pentavalent tungsten. After allowing the solution to equilibrate for 2 h, the sol was formed by adding water (0.05 ml) corresponding to an equimolar amount of tungsten. The gel was obtained by evaporating the solvent at ambient temperature.

### 2.2. Gel characterization

Chlorine in the unheated gel was qualitatively analyzed at ambient temperature using a Seiko SEA-3500 X-ray fluorescence analyzer equipped with an energy-dispersive solid state detector made of lithium-doped silicon. The X-ray diffraction spectrum was recorded at ambient temperature with a MAC Science MXP3 using graphite-monochromated Cu radiation. The IR spectrum was recorded at ambient temperature using a Perkin-Elmer 1600 FT–IR spectrometer; the unheated gel was dispersed in a KBr tablet. The Raman spectrum for the unheated gel was recorded at ambient temperature using a Nihon Bunko NR-1800 Raman spectrometer with an argon laser.

### 2.3. Thermal analysis

Simultaneous analysis of TG, DTA and MS was performed using a Rigaku 8101D thermal analyzer (TG/DTA) coupled with a Hewlett Packard 5890 mass spectrometer (quadruple type). The unheated gel was ground in an agate mortar before the thermal analysis. The sample (40.68 mg) was contained in a platinum crucible (5 mm  $\phi$   $\times$  2.5 mm). Alumina ( $\sim$  40 mg) was used as the reference material for the DTA. The sample was heated from ambient temperature to 750°C at a heating rate of 10°C min<sup>-1</sup> in helium flowing at a rate of 150 ml min<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Unheated gel

Chlorine was detected in the unheated gel by X-ray fluorescence analysis. The X-ray diffraction spectrum is shown in Fig. 1. The gel was amorphous with haloes at approx. 15° and 53°.

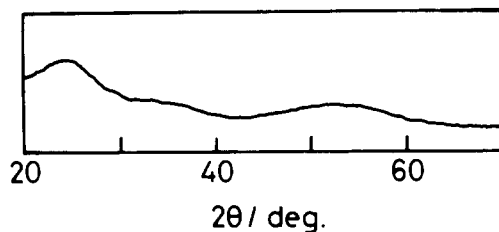


Fig. 1. X-ray diffraction spectrum for the unheated gel.

The IR spectrum is shown in Fig. 2. The absorptions at  $2897$  and  $1414\text{ cm}^{-1}$  are assigned to ethanolato. Ethanolato is expected to coordinate to the tungsten in the gel since the complex  $[\text{WCl}_3(\text{OC}_2\text{H}_5)_2]$  has been isolated from a reaction under the conditions similar to the gel preparation [11, 12]. The absorptions at  $3362$ ,  $3190$  and  $1616\text{ cm}^{-1}$  are assigned to water molecules [13]. The absorption at  $670\text{ cm}^{-1}$  and the shoulder at  $862\text{ cm}^{-1}$  are assigned to the stretching of O–W–O [13].

### 3.2. Thermal analysis

The TG, DTG and DTA of the gel are shown in Fig. 3. Four mass losses are observed at approx.  $40$ – $80$ ,  $130$ – $170$ ,  $190$ – $200$  and  $210$ – $600^\circ\text{C}$ . Corresponding to these mass losses, two endothermic peaks and two endothermic shoulders are observed. The TG curve is featureless above  $600^\circ\text{C}$ . The DTA shift above  $\sim 450^\circ\text{C}$  is interpreted as shrinkage or sintering of the tungsten oxide. The total mass loss after the thermal analysis from ambient temperature to  $750^\circ\text{C}$  was approx. 20.6%.

### 3.3. Mass spectra

The total ion current for  $m/z$  15–250 as a function of temperature is shown in Fig. 4. Four peaks corresponding to the thermal analysis were observed. An ion current for

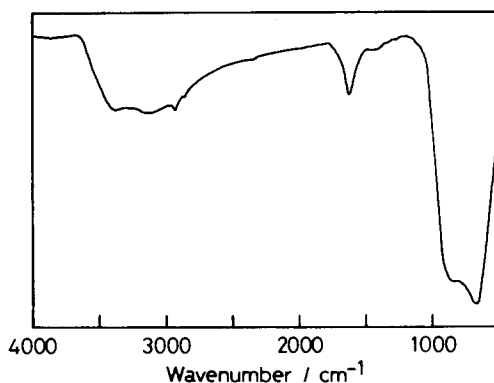


Fig. 2. IR spectrum for the unheated gel.

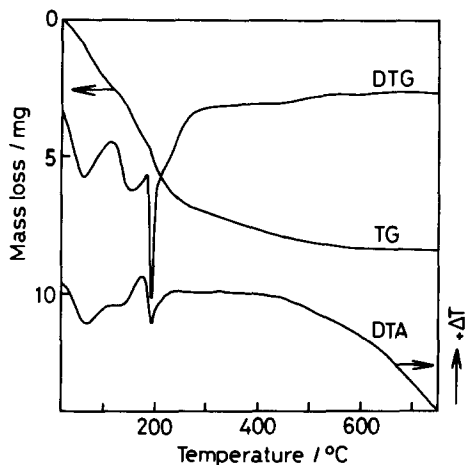
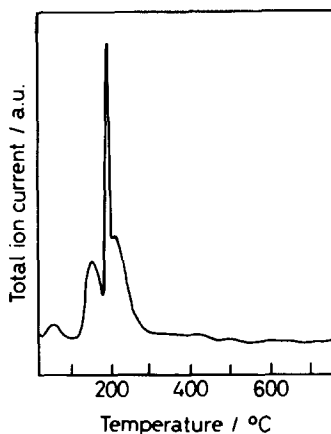


Fig. 3. TG, DTG and DTA of the gel.

Fig. 4. Total ion current for  $m/z$  15–250 as a function of temperature.

$m/z$  18 (water vapor) was detected only below  $100^{\circ}\text{C}$  which corresponded to the first endothermic mass loss.

An ion current of  $m/z$  28 is shown in Fig. 5. The peak profile corresponds to the second and third endothermic mass losses. Similar profiles were observed for  $m/z$  26, 27, 29, 49 and 64. They are ascribed to the fragments of ethylene ( $m/z$  28, 27 and 26) and chloroethane ( $m/z$  64, 49 and 29).

An ion current of  $m/z$  36 is shown in Fig. 6 whose peak profile corresponds to all the endothermic mass losses. Similar profiles were observed for  $m/z$  38, 37 and 35. They are ascribed to the fragments of hydrogen chloride. A mass spectrum due to chlorine ( $\text{Cl}_2$ ,  $m/z$  70, 72 and 74) was not detected.

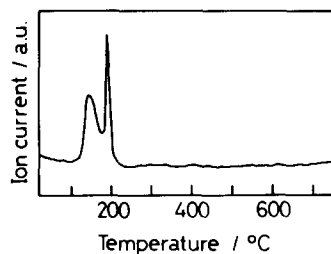


Fig. 5. Ion current for  $m/z$  28 as a function of temperature.

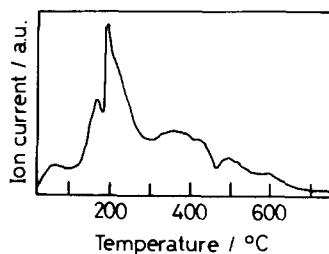


Fig. 6. Ion current for  $m/z$  36 as a function of temperature.

### 3.4. Firing process

The first endothermic mass loss is attributed to gas evolution of water vapor and a small amount of hydrogen chloride. The gas evolution is interpreted as vaporization of hydrochloric acid adsorbed on the gel. Hydrochloric acid and water were generated during the gelation. The existence of water molecules is supported by the IR spectrum of the unheated gel in which water molecules are not directly coordinated to tungsten.

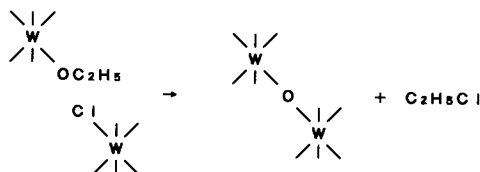
The second and third endothermic mass losses are attributed to the generation of ethylene, hydrogen chloride and chloroethane formed by reactions I and II shown in Fig. 7. The tungsten oxide may act as a catalyst. Both reactions occurred simultaneously because the relative amount of these gases was approximately constant. The stepwise (second and third) mass losses are explained by the different coordination sites (bond strength) of the ligands to the tungsten ions, i.e., in the equatorial and axial positions in the metal complex.

The fourth endothermic mass loss attributed to the evolution of hydrogen chloride. It is tentatively interpreted as follows; part of the hydrogen chloride evolved during the first, second and third endothermic mass losses adsorbed on the gel and then gradually desorbed as the fourth endothermic mass loss.

## 4. Conclusions

The firing process of an amorphous gel prepared by the sol-gel process using tungsten hexachloride was investigated by thermal analysis. Four endothermic mass

## Reaction I



## Reaction II

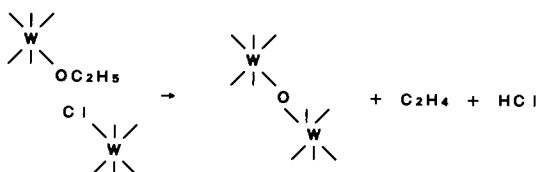


Fig. 7. Proposed decomposition reactions of the gel.

Table 1  
Summary of the endothermic mass losses

Step approx. temp °C		1st 40–80	2nd 130–170	3rd 190–200	4th 210–600
Evolved gases detected	H <sub>2</sub> O	○	×	×	×
	HCl	○	○	○	○
	C <sub>2</sub> H <sub>4</sub>	×	○	○	×
	C <sub>2</sub> H <sub>5</sub> Cl	×	○	○	×
Interpretation		Desorption of hydrochloric acid	Reactions I and II	Reactions I and II	Desorption of hydrogen chloride

losses were observed when heated in a helium flow from ambient temperature to 750°C. The results and the interpretation of the TG–DTA–MS are summarized in Table 1.

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