Synthesis and characterization of tungsten trioxide powders prepared from tungstic acids

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Abstract

WO3 powders were prepared by the thermal decomposition of tungstic acids (WO3–nH2O, n = 1/3, 1, 2). The tungstic acids were synthesized from WO42− aqueous solutions under a variety of conditions of pH, temperature and W(VI) concentrations. The thermal decomposition of the tungstic acids into WO3 was analysed by TG and DSC methods. Nano-sized WO3 powders with different morphological characteristics were obtained by thermal treatment of the tungstic acids at 500 °C in air atmosphere. The morphologies of WO3 powders were characterised by scanning electron microscopy and infrared absorption spectroscopy. Patterns of infrared spectra were related with distinct powder morphologies.

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1. Introduction

Tungsten trioxide (WO3) has been the subject of great interest due to its special electrochromic [1,2], gas sensing [3,4] and catalytic properties [5]. In these applications, the morphological characteristics of the materials like grain size or shape are very important and depend strongly on the preparation method. Therefore, WO3 has been prepared, both in the form of powders and thin films, by a plethora of methods which include chemical vapour deposition [6], sol-gel procedures [7], spray pyrolysis [8], and r.f. magnetron sputtering [9], among other methods.

Tungstic acids are well known compounds with the general formula WO3–nH2O. The synthesis of compounds with n = 1/3, 1/2, 1 or 2 has been reported [10–12]. The structure of tungstic acids [10–12] is composed of basic units of WO6 octahedra linked by shared corners, like in tungsten trioxide [12–14]
but in a more open framework. Solution methods involving tungstic acids as precursors have been reported, for example, the preparation of mesoporous WO₃ films using as precursor a colloidal solution of tungstic acid [15] and the synthesis of WO₃ by treatment of tungstic acid (WO₃·H₂O) with organic ligands or water-in-oil emulsions [16]. In this work, WO₃ powders were prepared by the thermal decomposition of tungstic acids (WO₃·nH₂O, n = 1/3, 1 or 2). These precursors were synthesised under a variety of conditions. The main purpose was to study the influence that the chemical route used to prepare WO₃ powders has on its morphological and structural characteristics.

The relation between infrared spectra and the size and shape of particles in microcrystalline powders has been described [17–21]. Powders composed of particles with known size and shape have been characterised by infrared spectroscopy and theoretical spectra were calculated based on the interpretation of surface mode absorptions [17–21]. Good fittings of the theoretical and corresponding experimental spectra were obtained. The lack of consistency among the reported infrared spectra of powdered corundum-type microcrystalline oxides was shown [18] to be due in part to the different particle shape of the samples used. In this paper the relation between morphology and the infrared spectra is explored for tungsten trioxide powders.

2. Experimental

2.1. Syntheses

Tungstic acids of general formula WO₃·nH₂O were synthesised using the methods of Freedman [10] (samples 1–7, 9 and 10) and Gerand et al. [11] (sample 8).

2.1.1. WO₃·2H₂O

2.1.1.1. Samples 1–6. To aqueous solutions of sodium tungstate was added hydrochloric acid 6.0 mol dm⁻³ with stirring at room temperature (20 °C). Sodium tungstate dihydrate (1.0 g) was dissolved in water (from 2 to 20 cm³) and different amounts of the HCl solution (from 4 to 20 cm³) were added in order to obtain different concentrations of the initial W(VI) species and H⁺ (Table 1). Yellow precipitates were formed. The precipitates were filtered, washed several times with water and dried at room temperature.

2.1.1.2. Sample 7. The above procedure was used with hydrochloric acid 0.25 mol dm⁻³ (500 cm³), that was added to an aqueous solution of sodium tungstate 1.0 mol dm⁻³ (10 cm³). The white precipitate obtained was filtered, washed several times with water and dried at room temperature. The white powder obtained was sensitive to sunlight and was kept in the dark.

2.1.1.3. Sample 8. To an aqueous solution of sodium tungstate 0.21 mol dm⁻³ (100 cm³) was added hydrochloric acid 1.0 mol dm⁻³ (50 cm³) with stirring at 5 °C. Both solutions were previously cooled to 5 °C and this temperature was maintained for two hours after mixing the solutions. A yellow gel was formed and washed with water by stirring and centrifuging. The gel obtained was dispersed in 4 dm³ of water and kept for two months at room temperature. Small yellow crystals were formed in the solution surface together with a yellow powder that settled down. Both solids were filtered and dried at room temperature.
2.1.2. WO$_3$H$_2$O

2.1.2.1. Sample 9. To an aqueous solution of sodium tungstate 1.0 mol dm$^{-3}$ (25 cm$^3$) was added hydrochloric acid 3.0 mol dm$^{-3}$ (225 cm$^3$) with stirring at 100 °C. Both solutions were previously heated to 100 °C and this temperature was maintained for thirty minutes after mixing the solutions. A dark yellow precipitate was formed. The precipitate was filtered, washed several times with water and dried at 100 °C for three hours.

2.1.3. WO$_3$1/3H$_2$O

2.1.3.1. Sample 10. To an aqueous solution of sodium tungstate 0.25 mol dm$^{-3}$ (100 cm$^3$) was added hydrochloric acid 1.0 mol dm$^{-3}$ (100 cm$^3$) with stirring at 100 °C. Both solutions were previously heated to 100 °C and this temperature was maintained for ten minutes after mixing the solutions. A white precipitate was formed. The precipitate was filtered, washed several times with water and dried at 100 °C for three hours. The white powder obtained was sensitive to sunlight and was kept in the dark.

2.2. Preparation of WO$_3$ powders

Tungsten trioxide was prepared by calcination of the tungstic acids, in air, at 500 °C over one hour (samples are designated as the respective tungstic acids (1–10) followed by C500).

2.3. Instrumentation

The X-ray powder diffraction (XRD) patterns were recorded using a Philips X’Pert instrument operating with Cu K$\alpha$ radiation ($\lambda = 1.54178$ Å) at 40 kV/50 mA. A JEOL JSM-35C scanning electron microscope was used to obtain the SEM images. Samples were prepared for microscopy by preparing a suspension of the powders in water, followed by slow evaporation on high-purity aluminium rods.
Infrared spectra were recorded on a Mattson Polaris FTIR spectrometer using pellets of 2 mg of the sample and 120 mg of spectroscopic-grade KBr. Thermogravimetric analysis was performed using a Mettler TG50 thermobalance and differential scanning calorimetry was measured on a Mettler DSC20 standard cell, both using heating rates of 10 °C/min. The solid state MAS NMR spectra were recorded using a Bruker MSL 400P spectrometer using TMS as the reference.

3. Results and discussion

3.1. Tungstic acids characterisation

Tungsten trioxide hydrates (tungstic acids, WO$_3$-$n$H$_2$O) with distinct hydration numbers ($n = 1/3$, 1 or 2) were obtained by changing conditions like temperature and, W(VI) or H$^+$ concentrations in a sodium tungstate aqueous solution. These compounds were isolated as crystalline powders (Table 1, samples 1–6 and 8–10) with the exception of an amorphous sample (7). All the crystalline samples were identified by X-ray powder diffraction. Typical SEM images for tungstic acids are shown in Fig. 1.

Tungsten trioxide dihydrates, WO$_3$·2H$_2$O, were prepared at room temperature using initial concentrations of H$^+$ from 0.25 to 4.0 mol dm$^{-3}$ (samples 1–8). Though the particle shapes are poorly defined, three different morphological patterns were clearly observed by performing SEM in WO$_3$·2H$_2$O particles: nano-sized “round plates” in samples 1–6 (Fig. 1a); agglomerated particles with undefined shape in the amorphous sample 7 (not shown); micrometric rectangular particles in sample 8 (Fig. 1b). In this sample, a longer time of crystallisation was employed resulting in bigger, well-defined particles. Tungsten trioxide monohydrate, WO$_3$·H$_2$O, was prepared at 100 °C using the initial H$^+$ concentration of 2.7 mol dm$^{-3}$ (sample 9). The SEM image of WO$_3$·H$_2$O particles (Fig. 1c) shows nano-sized “square plates”, with approximately the same size as WO$_3$·2H$_2$O particles in samples 1–6 but with a square morphology. The tungsten trioxide hydrate WO$_3$·1/3H$_2$O was prepared at 100 °C using the initial H$^+$ concentration of 0.50 mol dm$^{-3}$ (sample 10). The SEM image of WO$_3$·1/3H$_2$O (Fig. 1d) shows agglomerates of nano-sized particles, smaller than the WO$_3$·2H$_2$O or WO$_3$·H$_2$O particles (considering the nanosized range from 1 to 500 nm).

The infrared spectra of the tungstic acids are shown in Fig. 2. The strong absorption in the 500–900 cm$^{-1}$ region is assigned to the W–O vibrations such as in WO$_3$ [22,23]. The bands in the 3100–3550 cm$^{-1}$ region are assigned to the O–H stretching vibrations (asymmetric and symmetric) of coordinated water and the band at 1600 cm$^{-1}$ is assigned to the HOH bending of the coordinated water [24]. The WO$_3$·2H$_2$O spectrum (Fig. 2a) shows bands at 915, 940 and 1005 cm$^{-1}$. In this region, WO$_3$·H$_2$O (Fig. 2b) absorbs at 945 cm$^{-1}$ and in the WO$_3$·1/3H$_2$O spectrum (Fig. 2c) there are no distinct maxima. These bands are possibly due to the vibrations related with coordinated water, possibly with the W–OH$_2$ bond.

The thermal decomposition of the tungstic acids was monitored using TG and DSC methods (not shown). The $n$ value for each WO$_3$·$n$H$_2$O sample was calculated from the thermograms. WO$_3$·2H$_2$O dehydrates in two separate steps at 85 and 212 °C, respectively, loosing one water molecule at each temperature. WO$_3$·H$_2$O dehydrates at 222 °C, and WO$_3$·1/3H$_2$O dehydrates gradually in this range of temperatures. The DSC curves show an endothermic peak for each dehydration step at approximately the same temperatures obtained in the thermograms. An exothermic phase transition, at about 460 °C, was observed for the amorphous sample of WO$_3$·2H$_2$O (7) and WO$_3$·1/3H$_2$O.
Fig. 1. SEM images of WO$_3$\(\cdot\)H$_2$O particles. WO$_3$\(\cdot\)2H$_2$O: sample 3 (a) and sample 8 (b); WO$_3$\(\cdot\)H$_2$O: sample 9 (c) and WO$_3$\(\cdot\)1/3H$_2$O: sample 10 (d).
Expanded high-speed MAS NMR spectra of WO$_3$-$n$H$_2$O ($n = 1/3, 1, 2$) are shown in Fig. 3. All spectra display two sharp lines at 0.9 and 1.3 ppm with intensities which depend on the sample. These lines have no sidebands associated, even when relatively slow MAS rates (2–4 kHz) are used. This is illustrated in Fig. 4 for the case of WO$_3$H$_2$O. The sidebands observed are all associated with the broad resonance centred at 6.2 ppm. The broad peak is assigned to bulk water molecules coordinated to tungsten atoms and the sharp lines to two kinds of mobile surface hydroxyls. Spectral deconvolutions (carried out including the sidebands) show that the contribution of the hydroxyls to the total proton signal is estimated to be less than 5%. Based on variable temperature static $^1$H data of WO$_3$·1/3H$_2$O, others have previously assigned a Pake doublet to bulk coordinated water molecules and a sharper resonance to surface hydroxyls [25]. The MAS spectrum of WO$_3$·1/3H$_2$O shown in Fig. 3c displays two sharp lines at 0.9, 1.3 ppm and an ill-resolved shoulder at 2.5 ppm which we assign to three kinds of surface hydroxyls. Together they account for less than 5% of the total proton signal. The broad line (line width 1114 Hz) seen at 5.7 ppm is assigned to bulk water molecules. The resonance at 3.9 ppm is sharper (linewidth 563 Hz) than that at 5.7 ppm and it is probably due to adsorbed water. Indeed, its intensity was found to vary slightly from sample to sample. These two resonances have sidebands associated. Together, the hydroxyls and the adsorbed water account for over 30% of the total proton signal. This is in agreement with our TGA and FTIR data. The spectrum of WO$_3$·2H$_2$O (Fig. 3a) displays a broad line and traces of the two sharp peaks at low frequency (together much less than 1%).
It is not possible to simulate the broad spectral line with a single peak, two components (at least) centred at ca. 5.2 and 9.4 ppm must be considered. This would support the layered structure previously proposed for WO₃·2H₂O [26,27]. There are two kinds of bulk water molecules: those coordinated to the tungsten atoms in the layers and those in the space between the layers which are hydrogen bounded to the layers. We assign the signal at 9.4 ppm to the latter water molecules and the resonance at 5.2 ppm to the coordinated molecules.

3.2. Use of FTIR/SEM in WO₃ powders characterisation

Tungsten trioxide powders were prepared by calcination of the tungstic acids at 500 °C, in air. WO₃ powders with different morphologies were obtained. In general the WO₃ powders prepared from WO₃·2H₂O (samples 1C500 to 5C500, 7C500 and 8C500) showed similar morphologies to those of the powders before calcination (Figs. 5b and 1a, and Figs. 5c and 1b, respectively). The WO₃ powder prepared from WO₃·H₂O (sample 9C500) presents a different morphology from the powder before calcination (Figs. 5a and 1c, respectively) and as shown in Fig. 5a, the WO₃ powder obtained is composed of nano-sized ellipsoidal particles. The WO₃ powder prepared from WO₃·1/3H₂O (sample 10C500) also presents a different morphology from the powder before calcination (Figs. 5d and 1d, respectively); the WO₃ powder obtained is very agglomerated and sintering had already started as clearly seen in Fig. 5d. The initial WO₃·1/3H₂O powder was composed of nano-sized particles (Fig. 1d),
smaller than those of the other WO₃ hydrates, making sintering possible at a temperature as low as 500 °C. The presence of a few hexagonal shaped particles (Fig. 5d) may have its origin in the hexagonal structure of WO₃·1/3H₂O [11].

The infrared spectra of the WO₃ samples (Fig. 6) show a strong absorption between 600 and 1000 cm⁻¹ associated with the W–O–W stretching modes [22,23]. The weak infrared bands at 1010 and 1035 cm⁻¹ are assigned to the stretching of the W=O bonds at the surface [23], and are observed possibly due to the high surface area of these powders. WO₃ powders with different morphologies present different profiles of the infrared spectra in the strong absorption region (600–1000 cm⁻¹). Three distinct infrared band profiles can be defined, all presenting a very large absorption band resulting of overlapping of at least three bands, with: (A) maximum intensities at approximately 770 and 850 cm⁻¹ and a shoulder at 930 cm⁻¹, which have very similar intensities (sample 9C500, Fig. 6a); (B) distinct maximum intensities at approximately 740, 810 and 960 cm⁻¹, with respectively decreasing intensities (samples 1C500 to 5C500, Fig. 6b), also with a shoulder at 680 cm⁻¹ that can only clearly be seen in sample 8C500 (Fig. 6c); (C) a shoulder at approximately 630 cm⁻¹ and maximum intensities at 775 and 840 cm⁻¹, with respectively increasing intensities (samples 7C500 and 10C500, Fig. 6d). These IR band profiles (A–C) can be related with the powders morphologies using the SEM results: (A) nano-sized ellipsoidal particles (Fig. 5a); (B) flat particles, round (Fig. 5b) or rectangular shaped (Fig. 5c); (C) agglomerated particles with undefined shape (Fig. 5d).
Fig. 5. SEM images of WO$_3$ particles prepared by calcination of the tungstic acids WO$_3$·H$_2$O: sample 9C500 (a), WO$_3$·2H$_2$O: 3C500 (b), sample 8C500 (c); and WO$_3$·1/3H$_2$O sample 10C500 (d).
4. Conclusions

WO$_3$-$n$H$_2$O powders showing distinct morphological properties were obtained. The particles morphology of WO$_3$ prepared using the WO$_3$-$n$H$_2$O powders as precursors depends strongly on the precursors morphologies. Changes in the morphological characteristics of the WO$_3$ powders can be anticipated by analysis of the band profiles in the infrared spectra. Due to these features, this technique provides a straightforward method to evaluate in a first approximation the WO$_3$ particles morphology.

Fig. 6. Infrared spectra of WO$_3$ powders obtained by calcination of the tungstic acids WO$_3$H$_2$O: sample 9C500—IR profile A (a); WO$_3$2H$_2$O: sample 3C500—IR profile B (b), sample 8C500—IR profile-B (c) and WO$_3$1/3H$_2$O: sample 10C500—IR profile C (d).
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