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THERMAL BEHAVIOUR AND ANALYTICAL STUDY OF THE PRODUCTION OF $TiSnO_x$ FROM THE MIXED 8-HYDROXYQUINOLINATES

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Abstract

Solubility and pH precipitation studies were carried out to obtain the binuclear complex $\{[TiO(C_9H_6NO)_2][Sn(C_9H_6NO)_2]\}$ involving 8-hydroxyquinoline as chelating agent. The compound, the individual mononuclear complexes and their physical mixture were evaluated by means of techniques such as TG, DTA, elemental analysis, X-ray diffraction, IR spectroscopy. The properties of the original compounds and also the thermoanalytical conditions exerted a great influence on the degree of crystallinity and on the crystalline phase of the mixed oxide obtained as final product of the thermal decomposition.

Keywords: ceramic precursor, thermogravimetry, $TiSnO_x$

Introduction

Mixed oxides such as $TiSnO_x$ have been widely obtained from inorganic precursors and utilized as materials of technological interest either in electronic devices [1] or in gas sensors [2, 3].

One of the most commonly utilized techniques for the synthesis has been precipitation via hydrolysis of Ti(IV) and Sn(IV) in solution. The precipitate is then separated, dried and sintered in an electric oven for different periods of time, affording the mixed oxide as final product [1, 4–6]. Other techniques include preparation of a physical mixture of the individual constituent oxides [5, 6], a hydrothermal method [7], chemical vapour deposition [8] and ultrasonic spray pyrolysis [9].

The resulting mixed oxides have been characterized by checking the stoichiometry [1, 2], the crystalline phase [4, 8, 9], the corresponding kinetics of transformation [5, 9], the influence of the percentage of Sn(IV) ions on the unit cell dimensions [4, 5, 7, 8], the electrical conductivity [1], the morphology [1, 7–9] and the particle size [1, 7]. The physicochemical composition of the precursor powder, and the course of the reaction in the solid state, exert a considerable influence on the final properties of this kind of oxide.

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The aim of the present study was to obtain the mixed oxide $TiSnO_x$ via thermal decomposition of the precursor $\{[TiO(C_9H_6NO)_2][Sn(C_9H_6NO)_2]\}$, obtained by chemical precipitation, utilizing 8-hydroxyquinoline as complexing agent.

The effects of pH, the precipitation temperature, and the heating rate used during the thermal decomposition of the precursor on the final characteristics of the mixed oxides were evaluated.

Experimental

Preparation of the individual complexes

Bis(8-hydroxyquinolinate)oxotitanium(IV) was prepared by adding 0.71 mmol of titanium(IV) sulphate solution to 8-hydroxyquinoline (2.82 mmol) in an acetone-water medium (50:50). The pH and precipitation temperature were 5 and 5°C, respectively.

Bis(8-hydroxyquinolinate)tin(II) was prepared adding 0.60 mmol of tin(II) chloride to 8-hydroxyquinoline solution (2.41 mmol) in an acetone-water medium (50:50). The pH and precipitation temperature were 4 and 5°C, respectively.

The compounds found were:

$TiO(C_9H_6NO)_2{\cdot}H_2O$	found	N=7.43%, C=58.37%, H=3.81%
	calculated	N=7.57%, C=58.40%, H=3.27%.
$Sn(C_9H_6NO)_2$,	found	N=6.90%, C=52.37%, H=2.79%,
	calculated	N=6.88%, C=53.13%, H=2.97%.

Preparation of a precursor powder by physical mixing

$\{[TiO(C_9H_6NO)_2][Sn(C_9H_6NO)_2]\}{\cdot}H_2O$ was obtained as an equimolar physical mixture of the synthesized complexes $TiO(C_9H_6NO)_2{\cdot}H_2O$ (23.55 mmol) and $Sn(C_9H_6NO_2)$ (23.55 mmol).

Preparation of a precursor powder by chemical precipitation

$\{[TiO(C_9H_6NO)_2][Sn(C_9H_6NO)_2]\}$ was obtained through chemical precipitation, by the controlled addition from an automatic burette of 2.330 ml min^{-1} of a mixed solution containing equimolar amounts of tin(II) chloride and titanium(IV) sulphate to a solution of 2.76 mmol of 8-hydroxyquinoline in acetone-water (50:50).

The synthesis was performed in triplicate. Compounds TS4B1, TS4B2 and TS4B3 were obtained at pH 4 and 5°C. Compounds TS5A1, TS5A2 and TS5A3 were obtained at pH 5 and 40°C.

Characterization of the precursor powders

The X-ray powder diffraction patterns were obtained with an HGZ 4/B horizontal diffractometer in a Bragg-Bretano arrangement, with CoK_α radiation, a proportional counter and a pulse-height discriminator.

TG and DTA recordings were obtained by using an SDT 2960 thermoanalyser system (TA Instruments) with a synthetic air flux of 90 ml min^{-1}, a heating rate of 20 or 10°C min^{-1} and a sample mass of around 11 mg.

Elemental analyses were performed with a model EA 1110-CHNS-O (CE Instruments).

Table 1 Elemental analyses of the precursor powders (chemical precipitation)

Sample	Nitrogen(%)		Carbon(%)		Hydrogen(%)	
	found	calculated	found	calculated	found	calculated
TS4B1	7.23	6.97[a]	55.09	53.76	2.06	3.63
TS4B2	7.08		53.88		3.66	
TS4B3	6.85		51.95		3.69	
TS5A1	6.82	7.13[b]	51.93	55.00	3.68	3.46
TS5A2	7.23		52.42		3.57	
TS5A3	7.03	7.05[c]	52.75	54.37	2.69	3.55

a – calculated for $\{[TiO(C_9H_6NO)_2][Sn(C_9H_6NO)_2]\}\cdot 2.5H_2O$

b – calculated for $\{[TiO(C_9H_6NO)_2][Sn(C_9H_6NO)_2]\}\cdot 1.5H_2O$

c – calculated for $\{[TiO(C_9H_6NO)_2][Sn(C_9H_6NO)_2]\}\cdot 2H_2O$

Results and discussion

The synthesis conditions were suitable for the quantitative precipitation of the titanium(IV) and tin(II) complexes in a reaction medium of low solubility for these compounds and of high solubility for the 8-hydroxyquinoline ligand.

The TG curve for $TiO(C_9H_6NO)_2\cdot H_2O$ at 20°C min^{-1} (Fig. 1A) shows the first mass loss step between 40 and 139°C, with a corresponding endothermic peak in the DTA curve (Fig. 1A), which relates to dehydration of the compound. The anhydrous complex remains stable up to 300°C, when thermal decomposition of the ligand occurs in two steps up to 550°C. The DTA curve displays two exothermic peaks: the first at 300°C and the other, much more intense, at 510°C, with TiO_2 formation in the rutile phase at 1200°C, as revealed by the X-ray diffraction pattern (Fig. 3A).

The TG curve for $Sn(C_9H_6NO)_2$ at 20°C min^{-1} (Fig. 1B) demonstrates a mass increase between 218 and 233°C, with an exothermic peak at 228°C in the DTA curve (Fig. 1B), which corresponds to partial oxidation to the Sn(IV) complex.

Immediately after the oxidation, an endothermic peak can be seen at 238°C in the DTA curve, ascribed to fusion, followed by initial thermal decomposition with simultaneous partial volatilization of the complex, observed as exothermic and endothermic peaks of low intensity at 335 and 411°C, respectively. Above 500°C, mass loss occurs due to the thermal decomposition of the residual compound, with the formation of SnO_2 with an intense exothermic peak at 584°C.

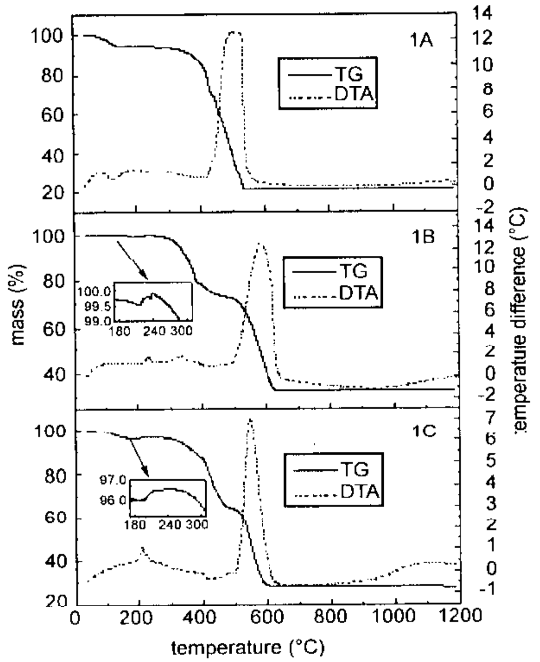

Fig. 1 TG and DTA curves of the individual complexes: 1A – $TiO(C_9H_6NO)_2 \cdot 1H_2O$ at 20°C min^{-1}; 1B – $Sn(C_9H_6NO)_2$ at 20°C min^{-1} and 1C – physical mixture at 10°C min^{-1}

The volatilization is reflected by the lower amount of SnO_2 at 1200°C (34.01%) relative to that estimated (37.02%). The SnO_2 formed corresponds to the rutile phase according to the X-ray diffraction pattern (Fig. 3B).

The TG curve of the mechanical mixture of the Ti(IV) and Sn(II) complexes (Fig. 1C) exhibits intrinsic characteristics of the individual compounds, such as a mass loss between 40 and 179°C, reflecting dehydration of the Ti(IV) complex, followed by a mass increase between 193 and 245°C, due to oxidation of the tin(II) complex.

Thermal decomposition of the ligand starts above 250°C, with an intense exothermic peak at 548°C in the DTA curve (Fig. 1C), with simultaneous volatilization of the tin(II) complex between 266 and 494°C, accompanied by a broad endothermic peak at 417°C. However, the metal loss is not significant: the amount of mixed oxide obtained (27.98%) is close to the estimated amount (29.67%). The X-ray diffraction pattern (Fig. 3C) suggests the formation of TiO_2–SnO_2 as a mixture of the rutile phases of its constituent oxides.

The TG and DTA curves of the mixed complexes synthesized by chemical precipitation (Figs 2A to 2D) illustrate the degree of repeatability for triplicate preparations, and the different thermogravimetric behaviour as regards both the different synthesis conditions (pH and temperature) and the different heating rates utilized to obtain the mixed oxides.

It can be observed that decrease of the heating rate for compounds TS4B does not effectively minimize the amount of material volatilized, due to: (i) the presence of the endothermic peaks at around 400°C in the DTA curve (Fig. 2B), which are characteristic of this reaction at 20 and 10°C min^{-1} , and (ii) the percentage of mixed oxide residue indicated in the TG curves (Fig. 2A): 22.89% at 20°C min^{-1} and 23.77% at 10°C min^{-1}, which are very close and much lower than the value estimated (28.67%) by taking into account the absence of this reaction.

The X-ray diffractograms of the residues obtained at 1200°C at 20°C min^{-1} (Fig. 3D) and 10°C min^{-1} (Fig. 3E) reveal the formation of mixed oxides $TiO_2 \cdot SnO_2$

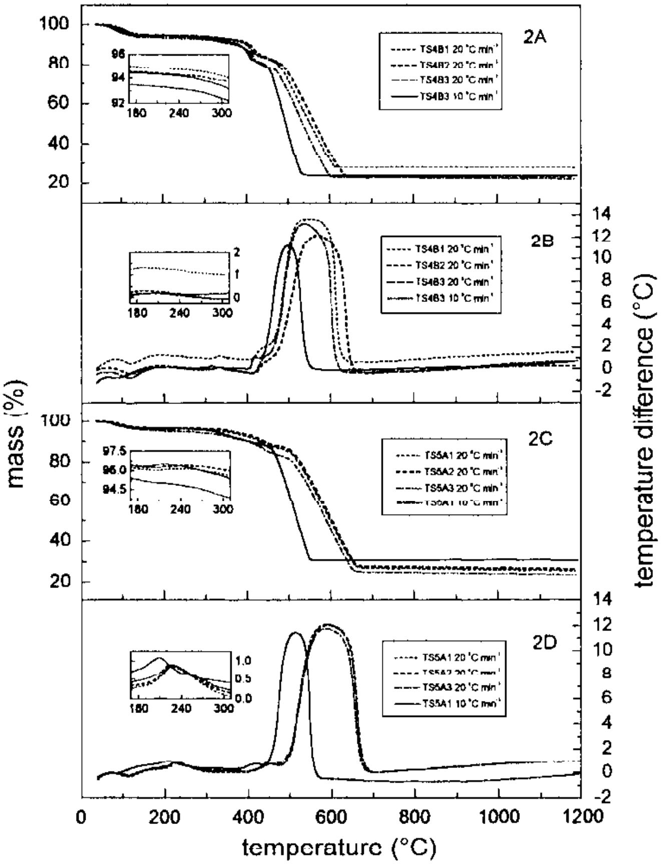

Fig. 2 TG and DTA curves of the precursor powders: 2A and 2B – TS4B compounds; 2C and 2D – TS5A compounds

in the rutile phase, similar to the TiO_2 in the same phase formed from the volatilization reaction.

In contrast, the DTA curves for TS5A (Fig. 2D) show no endothermic peaks characteristic of tin(II) complex loss. They exhibit exothermic peaks at around 220°C with a mass increase in the TG curves at 20 and 10°C min^{-1} (Fig. 2C), characteristic of the oxidation of the constituent tin(II) complex.

Decrease of the heating rate favours oxidation of the tin(II) complex at low temperatures. More oxide residue can be obtained (30.58%) than from the thermal decomposition at 20°C min^{-1} (26.76%), when there could have been a tin loss through volatilization of its complex, in spite of the absence of the endothermic peak at around 400°C, due to the superposition of the exothermic peaks from the ligand thermal decomposition.

Thus, it can be concluded that there is an inversely proportional relationship between the efficiency of the oxidation process for the tin(IV) complex and the amount of material volatilized; low heating rates are therefore necessary, so that the first reaction can be favoured.

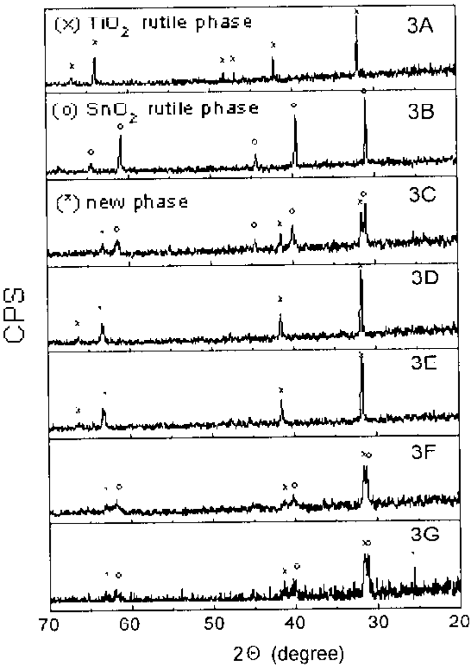

Fig. 3 XRD patterns of the individual and mixed oxides obtained from thermodecomposition up to 1200°C of the compounds: 3A $TiO(C_9H_6NO)_2\ 1H_2O$ at 20°C min^{-1}; 3B – $Sn(C_9H_6NO)_2$ at 20°C min^{-1}; 3C – physical mixture at 10°C min^{-1}; 3D and 3E – TS4B3 compound at 20 and 10°C min^{-1} respectively; 3F and 3G – TS5A1 compound at 20 and 10°C min^{-1} respectively

The X-ray diffractograms of the resulting mixed oxides $TiO_2 \cdot SnO_2$ (Fig. 3F and 3G) indicate no influence of the heating rate on the percentage of tin in the final product, since the thermal decomposition residues obtained at 10 or 20°C min^{-1} give the corresponding peaks for the interplanar distances close to those found for the oxide residue obtained from the mechanical mixture of the titanium(IV) and tin(II) complexes, in which the tin loss is minimal during heating (Fig. 3C).

This similarity means that the mixed oxide formed is a mixture of the rutile phase of its individual constituent oxides.

Conclusions

Preparation of the complexes via chemical precipitation was found to be a feasible method of obtaining mixed oxides $TiSnO_x$, and variation of the experimental conditions in the preparation and the thermal decomposition can lead to the formation of a different phase from that desired.

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