

Sn-Ce-O advanced materials obtained by thermal decomposition of some precursors

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The present work deals with the study of the thermal decomposition of tin and cerium precursors, in nonisothermal and isothermal conditions, in order to obtain Sn-Ce-O materials with different nominal Sn:Ce atomic ratio. The relation between precursor's ratio, thermal behaviour and phase composition of the end products has been investigated in order to establish the convenient thermal treatment for obtaining phases of interest. The methods used for the characterization of tin(II) oxalate and ammonium cerium(IV) nitrate, their mixtures and the end products have been simultaneous thermogravimetry and differential thermal analysis (TG/DTA), powder X-ray diffraction, IR spectroscopy and BET surface area measurements. Preferential formation of the cubic fluorite-type structure for samples with Sn:Ce atomic ratio ≤ 1 could be evidenced up to 600 °C.

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1. Introduction

Materials belonging to Sn-Ce-O system have opened new opportunities for their use in a wide variety of applications. Sensors obtained by doping of SnO₂ with CeO₂ present a good sensitivity, high selectivity and quick response to CH₄ and H₂S even at room temperature [1-2]. The redox properties of Sn_{1-x}Ce_xO₂ mixed oxides allowed their use as high-activity catalysts [3-5]. The compositions with CeO₂ content > 80 % mol. belonging to the SnO₂-CeO₂ binary system attracted interest for obtaining electrochromic layers exhibiting large optical transmission variation in UV, VIS and IR range [6]. Mixed CeO₂/SnO₂ film electrodes were used as photoanodes in a new generation of nanophase solar cells [7]. Tin dioxide-doped ceria materials are potential electrolytes for solid oxide fuel cells (SOFC) [8].

Peculiar properties required by these applications can be controlled by the structure and the morphology of the materials (phase composition, particle size, porosity and surface area) which depend on the initial oxide concentration, the thermal history and the method of preparation.

Azelee and Harrison [9] studied SnO₂-CeO₂ materials with different Sn:Ce atom ratios, thermally treated up to 1100 °C and no interaction between the two oxides was mentioned. Lin et al. [4] synthesized a variety of Ce_xSn_{1-x}O₂ mixed oxides and established that their structures depend on values of "x" and calcination temperature. Thus, when $x = 1.0 - 0.8$, Ce_xSn_{1-x}O₂ mixed oxides are in cubic phase; on decreasing "x" from 0.7 to 0.1 Ce_xSn_{1-x}O₂ mixed oxides are observed to have cubic and tetragonal mixed phases and single SnO₂ is in a tetragonal phase. Tolla et al. [10] studied the oxygen exchange properties in the new pyrochlore solid solution Ce₂Sn₂O₇ - Ce₂Sn₂O₈. The pure-phase cerium stannate

pyrochlore (Ce₂Sn₂O₇) has been prepared for the first time by solid state reaction of CeO₂, SnO₂ and metallic tin.

In our previous studies [11-16] Sn-Ce-O materials as reactive powders, films and porous ceramics have been obtained by different synthesis methods. The samples were characterized in terms of their structural, morphological and electrical properties. Depending on the specific precursor mixture, different microstructural parameters were obtained.

The present work deals with the study of the thermal decomposition of tin and cerium precursors in order to obtain Sn-Ce-O materials with different nominal Sn:Ce atomic ratio. The relation between precursor's ratio, thermal behaviour and phase composition of the end products has been investigated in order to establish the convenient thermal treatment for obtaining phases of interest.

2. Experimental

The raw materials were p.a. grade tin(II) oxalate (SnC₂O₄) (Fluka) and cerium(IV) ammonium nitrate (Ce(NH₄)₂(NO₃)₆) (Loba Feinchemie). The mixtures studied, with Sn:Ce atomic ratio = 39:1, 1:1 and 1:4, have been prepared by the classical ceramic method.

Simultaneous DTA and TG/DTG investigations were performed up to 1000 °C, in static air atmosphere, with α -Al₂O₃ as reference at a heating rate of 5°C min⁻¹. A MOM Budapest type Paulik-Paulik-Erdey Derivatograph OD-103 was used. Isothermal treatments, for one hour, at 400, 600 and 1000 °C of the samples were carried out in air, using a Nabertherm furnace. X-ray diffractograms have been recorded for the samples resulting from non-isothermal treatments with a HZG-4 (FPM-Zeiss) Diffractometer using Cu K α radiation ($\lambda = 1.54056$) with Ni filter and for the samples isothermally treated with a DRON UM 1 Diffractometer using Co K α radiation ($\lambda = 1.79021$). IR

spectra were recorded in 4000–200 cm^{-1} range with a Carl Zeiss Jena Specord 80 Spectrophotometer. Specific surface area measurements were performed by BET method.

3. Results and discussion

3.1. Nonisothermal treatments

Nonisothermal treatments of the studied samples were performed in air up to 1000 °C. DTA and TG/DTG curves of the studied mixtures are presented in Figs. 1 and 2. The decomposition of both precursors (SnC_2O_4 and $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$) takes place in the same temperature range (200–400 °C) and the thermal behaviour of the mixtures depends on their initial composition. Thus, DTA curve of the sample 1-ON (Fig. 1), which contains only 2.5 % at. Ce, exhibits the exothermal combustion effect of the main precursor (tin(II) oxalate), at 350 °C. Supplementary, one can observe two exothermal effects due to the presence of $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ and SnO oxidation [14].

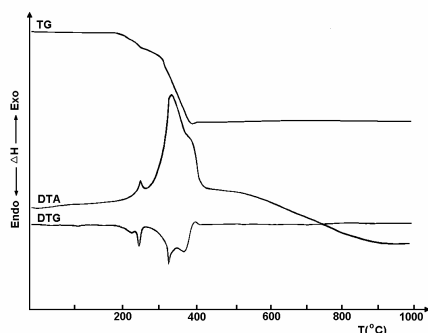
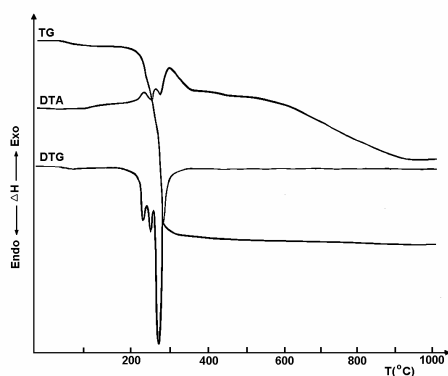
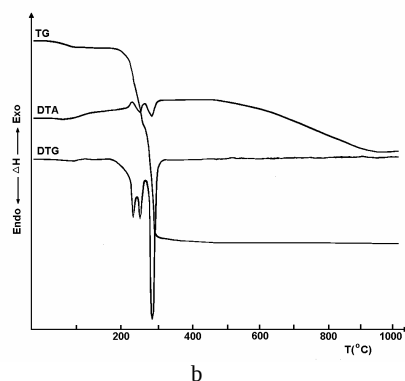


Fig. 1. Thermal behaviour of initial mixture 1-ON.

Thermal analysis curves of the mixtures 2-ON and 3-ON are similar (Figs. 2a and 2b). However, DTA curve of the mixture 2-ON shows a supplementary exothermal effect at 290 °C assigned to the SnC_2O_4 combustion, shifted with ~ 80 °C to lower temperature.



a



b

Fig. 2. Thermal behaviour of initial mixtures: a) 2-ON and b) 3-ON.

Table 1 presents the Sn:Ce atomic ratio and the total weight losses due to the thermal decomposition of the starting mixtures.

Table 1. TG data of the studied samples.

Sample	Sn:Ce atomic ratio	Weight loss (%)	
		Exp.	Calc.
1-ON	39:1	31.84	29.74
2-ON	1:1	60.59	57.24
3-ON	1:4	68.9	65.13

The weight loss was calculated considering SnO_2 and CeO_2 as final products of the nonisothermally treated compositions.

X-ray diffraction patterns of the DTA/TG residues, presented in Figure 3, show, according to the initial atomic ratio of Sn and Ce, a different phase formation.

X-ray data indicate the presence of only one phase for the sample 1-ON (SnO_2 with a rutile-type structure) and for the sample 3-ON (CeO_2 with a fluorite-type structure). For the sample 2-ON one can notice the presence of the both rutile- (with a lower crystallization degree) and fluorite-type phases. Compared to the ASTM files for SnO_2 (file 21-1250) and CeO_2 (file 75-0390) a shift of the diffraction lines to larger angular values for the studied samples was noticed.

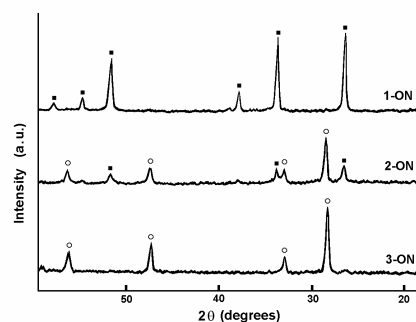


Fig. 3. X-ray diffraction patterns ($\lambda = 1.54056$) of the samples nonisothermally treated up to 1000 °C: ■ - SnO_2 ; ○ - CeO_2 .

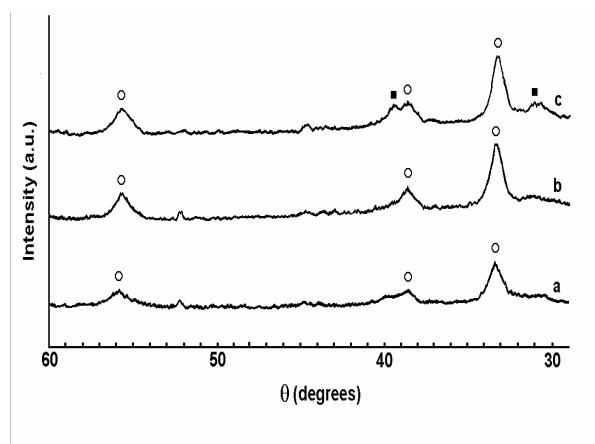


Fig. 4. X-ray diffractograms ($\lambda = 1.79021$) of the sample 2-ON isothermally treated/1h at: a) 400 °C, b) 600 °C and c) 400 °C + 600 °C; ■ - SnO_2 ; ○ - CeO_2 .

IR spectra of the initial mixtures and of the residues of the mixtures after thermal treatment at 1000 °C were recorded. In comparison with the initial mixtures, the IR spectra of the samples nonisothermally treated up to 1000 °C show the vanishing of the oxalate, ammonium and nitrate groups but the presence of the SnO_2 and/or CeO_2 characteristic bands, according to Sn:Ce atomic ratio.

IR spectrum of the sample 1-ON exhibits only the characteristic vibration band of SnO_2 lattice (700-600 cm^{-1}). The flattening of the peak situated at 680 cm^{-1} could be due to CeO_2 inclusion into SnO_2 matrix [15]. Fig. 5 presents IR spectra of the samples 2-ON and 3-ON nonisothermally treated up to 1000 °C.

IR spectrum of the sample 2-ON (equimolar initial mixture of SnC_2O_4 and $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$) shows both the characteristic bands of SnO_2 and CeO_2 lattice. For the sample 3-ON only the characteristic band of CeO_2 , in the 600-300 cm^{-1} range was evidenced, even if SnO_2 content is 20 % mol. A good agreement between IR spectroscopy results and X-ray diffraction data can be mentioned.

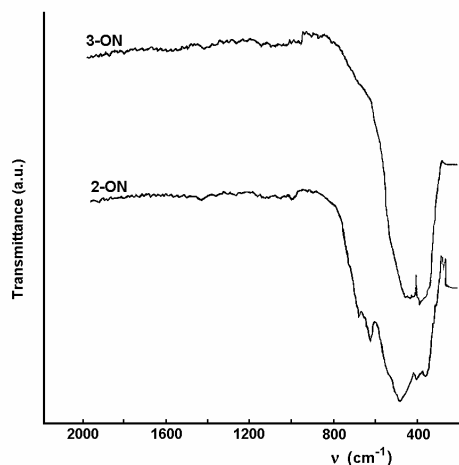


Fig. 5. IR spectra of the samples 2-ON and 3-ON nonisothermally treated up to 1000 °C.

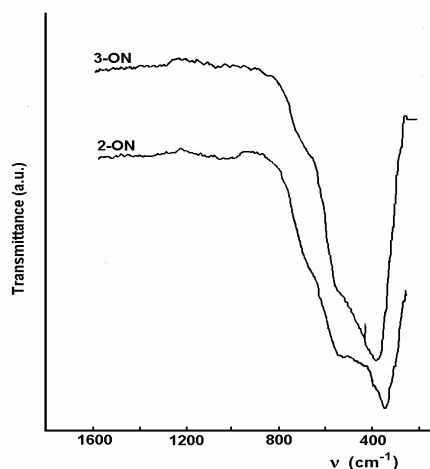


Fig. 6. IR spectra of the samples 2-ON and 3-ON isothermally treated at 400 °C/1h.

3.2. Isothermal treatments

Samples 1-ON, 2-ON and 3-ON were isothermally treated in air at 400 °C for one hour, taking into account DTA/TG data, which indicated the complete decomposition of the mixtures up to this temperature. X-ray diffraction patterns exhibit for all samples broad peaks, situated on the positions of characteristic lines of the tetragonal structure (for the sample 1-ON) and cubic structure (for the samples 2-ON and 3-ON). This fact indicates a low crystallinity degree of all samples. Also, IR spectra of the samples 2-ON and 3-ON isothermally treated at 400 °C for one hour, presented in Fig. 6, indicate only the formation of a disordered cubic-type structure, better developed for the sample 3-ON.

Particular specific surface area values, obtained by BET measurements are summarized in Table 2.

Table 2. Morphological characteristics of the studied samples, thermally treated at 400 °C for one hour.

Sample	Phase composition	Surface area m^2/g
1-ON	SnO_2 low crystallinity	16.5
2-ON	CeO_2 low crystallinity	58
3-ON	CeO_2 low crystallinity	40

Our characterization methods pointed out a special behavior of the sample 2-ON. X-ray diffraction pattern did not indicate the solid solution with fluorite-type structure formation in the case of sample 2-ON. The tin dioxide content, although equal with the cerium dioxide one, was not evidenced nor by X-ray diffraction neither by IR spectroscopy. For this Sn:Ce atomic ratio (1:1), Tolla et al. [10] obtained a $\text{Ce}_2\text{Sn}_2\text{O}_7$ pyrochlore phase using as starting materials CeO_2 , SnO_2 and Sn in appropriate

amounts, the Sn(IV)/Sn(O) ratio being fixed in order to reduce all the Ce(IV) cations to Ce(III).

The experimental conditions of the tin(II) oxalate decomposition could lead to the formation of SnO which turns into SnO₂ and Sn metallic. Moreover, the pyrochlore-type structure (P.G. Fd3m) is related to that of CeO₂ fluorite (P.G. Fm3m). Therefore, we thermally treated the sample 2-ON at 600 °C, for one hour, in order to check if the disordered cubic structure obtained at 400 °C turns into a pyrochlore structure. X-ray diagrams of the isothermally treated for one hour sample 2-ON, at 400 °C (case a) and 600 °C (case b) were similar but the X-ray diagram of the sample 2-ON, isothermally treated for one hour, first at 400 °C and then at 600 °C (case c), shows the beginning of the SnO₂ lattice ordering (Fig. 4). Probably in cases a) and b) tin dioxide was still amorphous phase and that is why tetragonal SnO₂ lattice (rutile-type) was not identified by X-ray diffraction and IR spectroscopy. One can mention that ~5 nm size SnO₂ particles were obtained by Uematsu [17] by the thermal decomposition of tin(II) oxalate.

The isothermal treatment at 1000°C evidenced for the sample 1-ON the presence of only one SnO₂ phase with tetragonal structure and for the samples 2-ON and 3-ON the presence of both phases SnO₂ (rutile-type structure) and CeO₂ (fluorite-type structure).

4. Conclusions

DTA and TG/DTG data pointed out that, for all studied samples, thermal decomposition is complete up to 400 °C. Rutile-type phase (SnO₂) and/or fluorite-type phase (CeO₂) were identified phases for the nonisothermal end products, according to the initial composition.

Representative samples were thermally treated in isothermal conditions at 400 °C, 600 °C and 1000 °C. Only one fluorite-type phase (CeO₂), with a disordered structure, was identified for the samples with Sn:Ce atomic ratio ≤ 1 up to 600 °C. At 1000 °C, both phases SnO₂ (rutile-type structure) and CeO₂ (fluorite-type structure) were evidenced. No ternary oxide phases are formed at this temperature.

Preferential ordering of the cubic fluorite structure of CeO₂, SnO₂ remaining as amorphous phase up to 600 °C, recommends these materials as high-activity catalysts.

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