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Thermal properties of multinuclear Ti(IV) and Zr(IV) carboxylate derivatives characterized using thermal analysis and variable temperature MS and IR methods

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Studies of the thermal properties of multinuclear Ti(IV) and Zr(IV) carboxylates with general formulas $[Ti_8O_8(O_2CBu^t)_{16}]$ and $[Zr_6O_4(OH)_4(O_2CBu^t)_{12}]$ which can be used as potential source compounds in producing TiO_2 and ZrO_2 thin layers, were carried out. Thermogravimetric methods (TG/DTG/DTA), mass spectrometry (MS-EI), and variable temperature infrared spectroscopy (VT-IR) were used to determine the thermal decomposition pathway, identify volatile titanium and zirconium species in vapours, and determine their thermal stability. The applications of Ti(IV) and Zr(IV) compounds in MOCVD experiments as potential metal oxide precursors are discussed.

Key words: *Ti(IV) carboxylates; Zr(IV) carboxylates; thermal decomposition; IR spectroscopy; mass spectrometry*

1. Introduction

The substitution of alkoxy groups in Ti(IV) and Zr(IV) alkoxides ($M(OR)_4$, $R = Et, Pr^i, Bu^n$) by bidendate carboxylate ligands (O_2CR', $R' = MC, Bu^t, CH_2Bu^t$) is used to moderate the reactivity of alkoxides in sol-gel processing [1–4] and to introduce organic functionalities [5]. Several multinuclear Ti(IV) and Zr(IV) oxo carboxylates and their complexes with alkoxides can be isolated from stoichiometric reactions of $M(OR)_4$ with carboxylic acids [3, 4, 6, 7]. The source of oxo ligands are water molecules produced during the esterification process of excess acid with liberated alcohol.

In our previous works, we have focused on the structural and spectral characterization of titanium(IV) compounds [6, 7]. Analysis of these data suggests that selected

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multinuclear oxo complexes show promising properties as sources of volatile titanium species for the deposition of TiO_2 layers by CVD techniques [6, 10]. Therefore, such problems as: (a) the volatility of titanium and zirconium compounds, (b) their thermolysis pathway, (c) the composition of the gas phase, and (d) the stability of volatile metallic species transported in vapours, should be investigated in detail.

In the presented report, the results of thermal analysis and temperature variable mass spectrometry (MS) and IR studies for Ti(IV) and Zr(IV) compounds of general formulas $[Ti_8O_8(OOCBu^t)_{16}]$ (1) and $[Zr_6O_4(OH)_4(O_2CBu^t)_{12}]$ (2) are described. Moreover, the results of CVD experiments are discussed.

2. Experimental

Syntheses of **1** and **2** were carried out under argon atmosphere using standard Schlenk line and glovebox techniques as reported in literature [4, 7]. Microanalysis, ^{13}C NMR, ^{1}H NMR, and infrared (IR) methods were used to confirm their structure. Both compounds were stored at room temperature under argon atmosphere.

IR spectra were recorded with an FT-IR SPECTRUM 2000 spectrometer. Variable temperature IR spectroscopic studies in the solid phase were carried out with a SPECAC temperature variable cell. IR spectra of vapours transported with the carrier gas (Ar) were studied in a specially constructed reactor, presented in Fig. 1. Thermogravimetric analysis (TGA) was carried out using SDT 2960 TA Instruments, in nitrogen atmosphere from 298 to 773 K and at the ramp rate of 3 K·min^{-1}. Mass spectra were measured with an MS AMD-604, MASPEC system using the EI method.

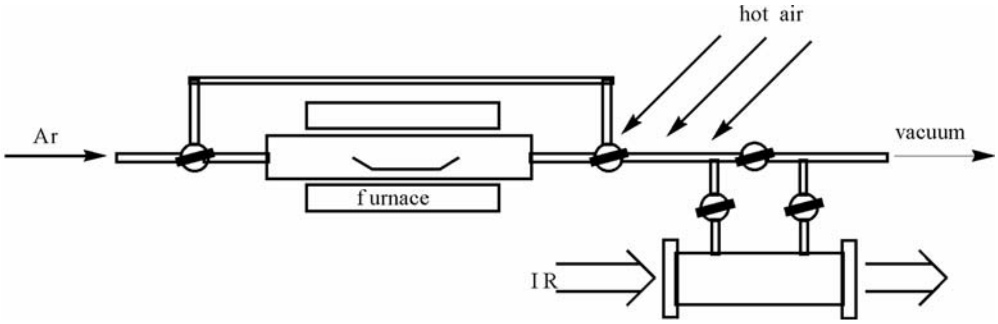

Fig. 1. Schematic diagram of the reactor used for variable temperature IR experiments

Deposition experiments were carried out using a horizontal "cold-wall" CVD reactor with the volume of 10 dm^3, heated substrate electrode on top, 56 mm in size, a gas input shower from a distance of 15 mm and with a gas flow of 60 cm^3·min^{-1}. The morphology of the metal oxide films was studied with a scanning electron microscopy (JSM 5500LV) and EDXS system.

3. Results and discussion

The colourless crystals of $[Ti_8O_8(OOCBu^t)_{16}]$ (**1**) and $[Zr_6O_4(OH)_4(O_2CBu^t)_{12}]$ (**2**) were synthesized by slow evaporation (glovebox) from a 1 : 2 mixture of $M(OPr^1)_4$ (M = Ti(IV) and Zr(IV)) and $HOOCBu^t$ in toluene and *n*-hexane for **1** and **2**, respectively. Crystallographic and spectral studies [4, 7] revealed that the structures of these compounds consist of $\{Ti_8(\mu_2–O)_8\}$ and $\{Zr_6(\mu_3–O)_4(\mu_3–OH)_4\}$ clusters stabilized by carboxylate ligands. Multinuclear titanium(IV) or zirconium(IV) oxo carboxylate molecules are associated through a network of weak van der Waals inter-molecular interactions. This is a promising feature in terms of volatility and suitability as a CVD precursor.

The thermal decomposition of the above compounds was studied using thermogravimetric and differential thermal analysis (TG/DTA/DTG) methods over the temperature range of 298–873 K with a heating rate of 3 K/min under the nitrogen atmosphere. The TGA/DTA/DTG data of **1** have shown that thermal decomposition proceeds in three endothermic stages: 298–589 K, 589–658 K, and 658–738 K, with a weight loss of 73.4%. According to our structural reports [7], the endothermic effect between 298 and 589 K can be explained by the detachment of solvent molecules (toluene) from the crystalline lattice of this compound. During the decomposition process, **1** undergoes a complete conversion to TiO_2 (above 589 K), as was confirmed by X-ray powder diffraction studies. According to thermogravimetric studies, crystals of **2** are stable in N_2 up to 433 K. The multi-step thermal decomposition of this compound proceeds in four endothermic stages: 433–533 K, 623–693 K, 693–757 K, and 757–803 K (weight loss: 60.9%). The final product of decomposition was ZrO_2, and its presence in solid residue was confirmed by X-ray powder diffraction.

The composition of vapours formed during the thermolysis of Ti(IV) and Zr(IV) oxo carboxylate derivatives, and the thermal stability of volatile metallic species were assessed on the basis of MS-EI spectra recorded between 423 and 623 K. According to these data, the following characteristic peaks were found in the spectra of **1**: at m/z = 2027 ($[Ti_8O_8(O_2CBu^t)_{15}]^+$) and m/z = 1554 ($[Ti_8O_8(O_2CBu^t)_{10}]^+$), and in the spectra of **2**: m/z = 1913 ($[Zr_6(OH)_8(O_2CBu^t)_{11}(O_2CC_3H_3)_2]^+$), m/z = 1757 ($[Zr_6O_3(OH)_3(O_2CBu^t)_{11}]^+$), and m/z = 1573 ($[Zr_6O_2(OH)_4(O_2CBu^t)_9]^+$). The stability of multinuclear oxo species has been studied on the basis of the temperature dependence of peak intensity (Fig. 2).

In the case of **1**, the intensity of peaks assigned to titanium-containing fragments was very low below 423 K, which indicates the thermal stability of titanium oxide clusters (Fig. 2a). At the threshold temperature, about 423 K, an increase in the intensity of the m/z = 2027 ($[Ti_8O_8(O_2CBu^t)_{15}]^+$) peak and a simultaneous decrease in the decomposition product peaks (m/z = 1554, $[Ti_8O_8(O_2CBu^t)_{10}]$) are observed. According to these data, the concentration of multinuclear Ti(IV) oxo carboxylate derivatives in vapours is the highest between 513 and 533 K. The thermal stability of these species is low, and their rapid decomposition above 533 K is observed. Similar effects are noticed in thee variable temperature MS spectra of **2** (Fig. 2b). Between 543 and

573 K, however, the decomposition products containing volatile multinuclear zirconium fragments are formed at higher temperatures. Also in this case the thermal stability of these patterns is low, and their decomposition is noticed above 573 K.

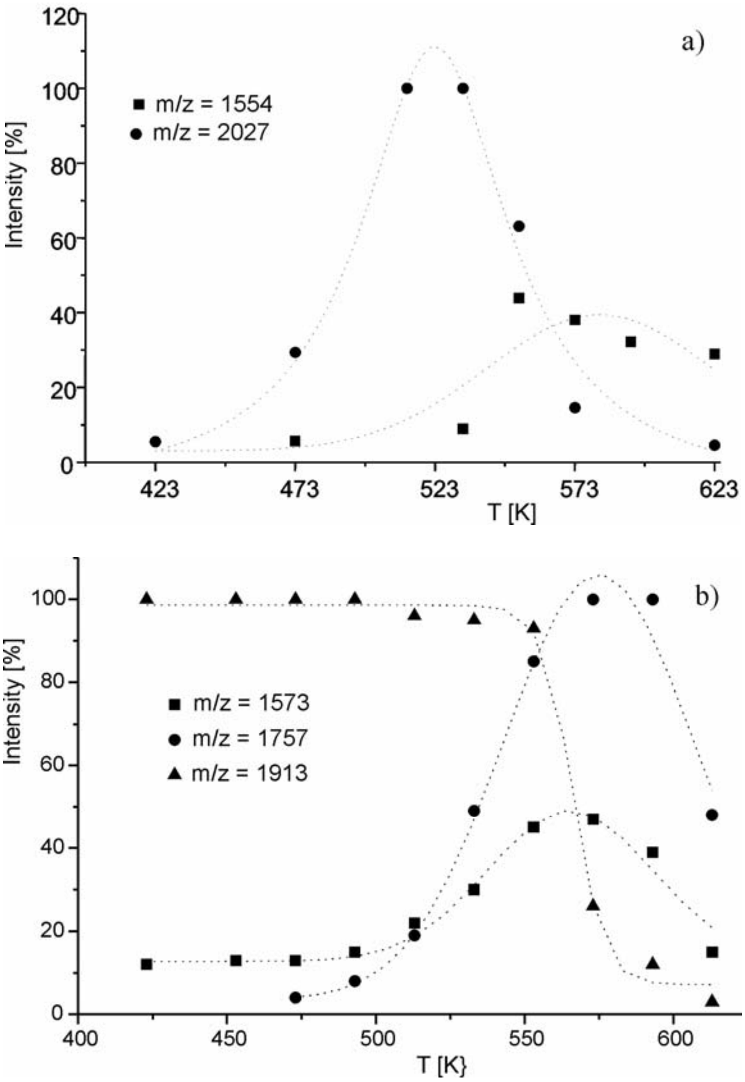

Fig. 2. Results of MS-EI investigations for a) $[Ti_8O_8(O_2CBu^t)_{16}]$ (**1**) and b) $[Zr_6O_8(O_2CBu^t)_{12}]$ (**2**). Variations in the intensity of selected peaks with temperature (m/z = 1554 for $[Ti_8O_8(O_2CBu^t)_{15}]^+$, m/z = 2027 for $[Ti_8O_8(O_2CBu^t)_{10}]^+$, m/z = 1573 for $([Zr_6O_2(OH)_4(O_2CBu^t)_9]^+)$, m/z = 1757 for $([Zr_6O_3(OH)_3(O_2CBu^t)_{11}]^+)$, and m/z = 1913 for $([Zr_6(OH)_8(O_2CBu^t)_{11}(O_2CC_3H_3)_2])^+)$

In order to find another way of characterizing the thermal decomposition pathway of the studied compounds, we have applied variable temperature IR spectroscopy (VT-IR) to the vapours evolved during the above process. The thermal analyser was connected with the FT-IR instrument and the vapours were transported to the spectrometer chamber, providing the spectra of gaseous products (Fig. 1). The appearance of bands attributed to the vibrations of coordinated carboxylate groups (ν_{as}(COO) = 1520–1600 cm^{-1}) and metal-oxide bridges (ν_{as}(MOM) = 600–800 cm^{-1}) has been used to identify volatile metal-containing species. The temperature variable IR spectra of **1** and **2** are presented in Figs. 3 and 4.

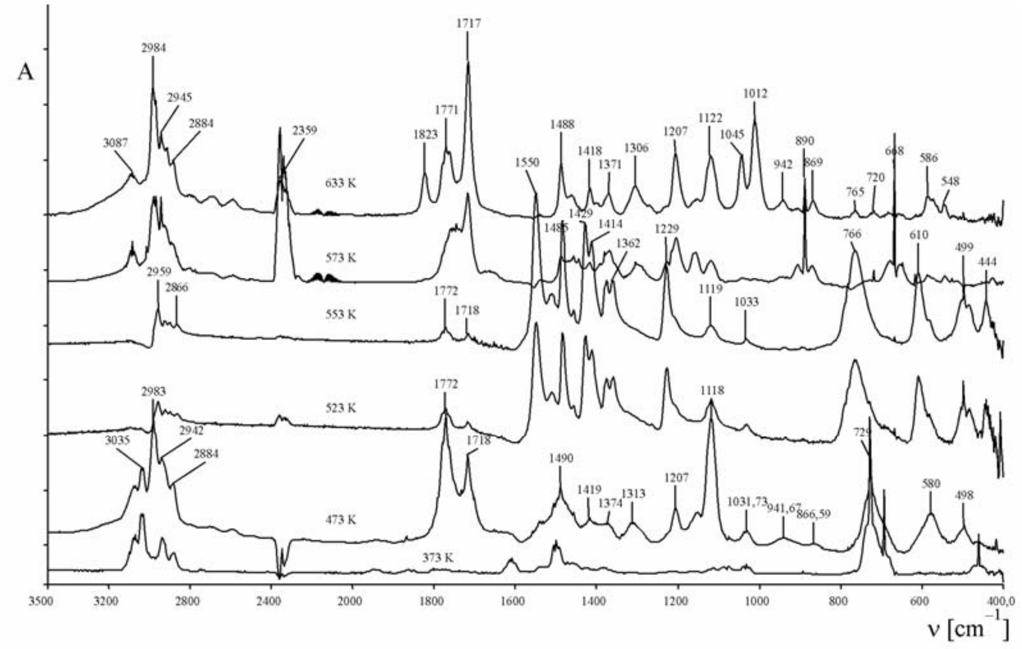

Fig. 3. Variable temperature IR spectra of vapours formed during the thermal decomposition of **1**

An analysis of the VT-IR spectra of **1** (Fig. 3) revealed that three types of volatile species are formed during the three decomposition stages, which confirms the results of thermogravimetric studies [7]. The appearance of absorption bands at 3035, 1610, 1490, and 729 cm^{-1} in spectra recorded below 523 K proves that toluene molecules are detached from the crystal lattice in the first stage of the thermal decomposition of **1**. Simultaneously, the partial decomposition of these compounds accompanies an increase of the intensity of bands at 1772, 1718, 1118, 580, and 498 cm^{-1} in the temperature range of 373–523 K. Stable volatile titanium species, containing multinuclear oxo clusters and stabilized by carboxylate ligands, were detected between 523 and 553 K (with bands at 1550 and 1429 cm^{-1} assigned to the vibration of carboxylate bridges, and at 766 cm^{-1} to the vibration of Ti–O–Ti bridges). The characteristic bands attributed to CO_2 (2359, 668 cm^{-1}), CO (2169, 2105 cm^{-1}), $(RCO)_2O$ (1823, 1771 cm^{-1}), and RCOOR′ (1717 cm^{-1}) were observed in the high-temperature IR spectra. This indicates a higher degree of decomposition, which occurs at temperatures above 553 K.

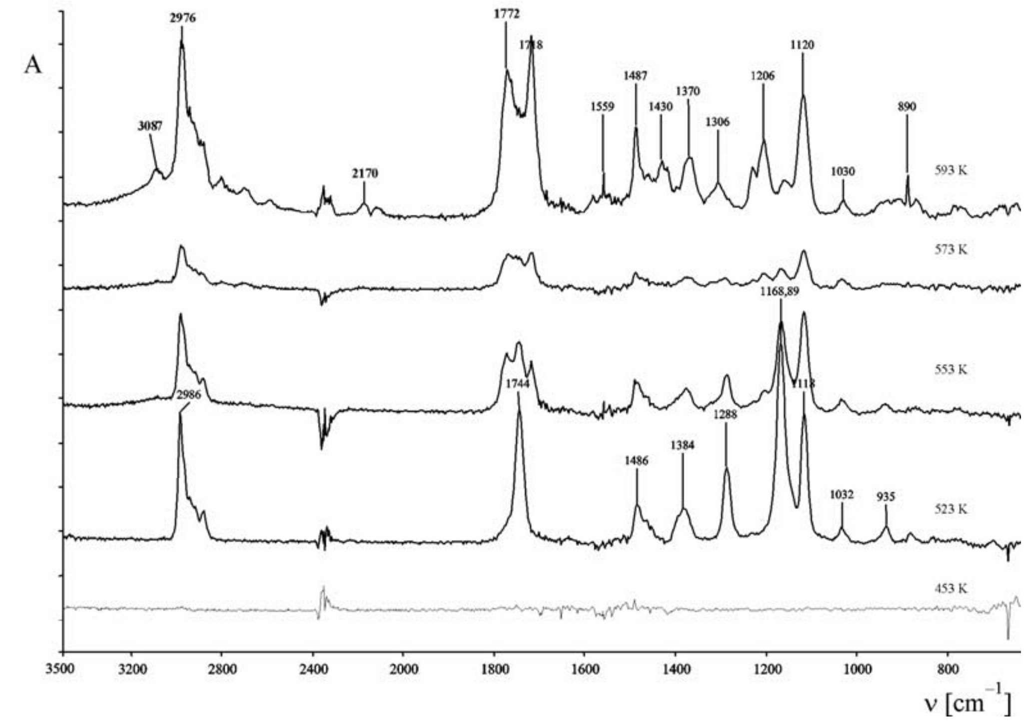

Fig. 4. Variable temperature IR spectra of vapours formed during the thermal decomposition of **2**

VT-IR studies of **2** (Fig. 4) indicate the high thermal stability of this compound between 453 and 593 K. Only bands assigned to volatile organic products, formed during the thermal decomposition of this compound, were observed between 523 and 593 K. Absorption bands, which could be the evidence of the presence of volatile zirconium-containing fragments (e.g. attributed to the vibrations of Zr–O–Zr or coordinated COO groups), were not detected in the IR spectra of the vapours.

Despite the lack of strong intermolecular association of metal-oxide clusters in the crystal lattice, variable temperature MS and IR experiments show that **1** and **2** are characterized by a high thermal stability under the studied conditions. This is a negative feature in terms of the volatility and suitability of CVD precursors. However, the formation of volatile and stable multinuclear titanium oxo clusters in the narrow temperature range of 523–553 K in the case of **1** is possible. Therefore, *cold-wall* CVD experiments using $[Ti_8O_8(O_2CBu^t)_{16}]$ as a TiO_2 precursor were carried out. Thin TiO_2 films (the thickness of layers was below 100 nm) were deposited on Si(111) substrates in the temperature range of 873–923 K, under a total reactor pressure of 2 mbar (vaporization temperature T_V was 523 K). Scanning electron microscopy (SEM) studies of film morphologies show dense and smooth textures for films grown from this compound between 673 and 923 K (Fig. 5). The composition of this film was established by the EDXS analysis. The films are composed mainly of titanium and oxygen atoms. X-ray diffraction (XRD) studies revealed that amorphic films of TiO_2 are formed.

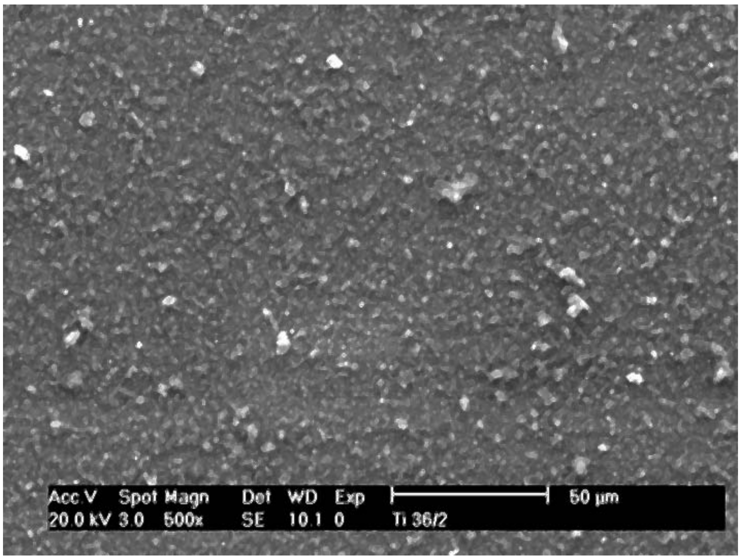

Fig. 5. SEM microphotograph of the film
deposited from **1** using the "cold-wall" CVD method

4. Conclusions

Studies of $[Ti_8O_8(O_2CBu^t)_{16}]$ (**1**) and $[Zr_6O_4(OH)_4(O_2CBu^t)_{12}]$ (**2**) proved high thermal stability of these compounds. Thermal decomposition proceeds by the conversion of **1** and **2** to TiO_2 and ZrO_2, which was confirmed by XRD methods for the solid residue. An analysis of the variable temperature IR spectra of vapours revealed that esterification and decarboxylation products are the main gas phase components. However, the volatile and stable multinuclear titanium oxo clusters can also be formed during the thermal decomposition of **1** between 523 and 553 K. The thermal stability of these fragments is suitable for their transport in the gas phase, which is a positive feature for the application of **1** as a CVD precursor. The results of "cold -wall" CVD experiments showed that the deposition of thin (< 100 nm) amorphic TiO_2 films is possible.

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