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Synthesis of titanium dioxide nanocrystalline layers using hexaprismatic shaped μ-oxo Ti(IV) alkoxo carboxylates as precursors

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ABSTRACT

The reaction between $Ti(OR)_4$ (R = ^{n}Bu, ^{i}Bu, $SiMe_3$) and 2,2-dimethylpropionic acid lead to the formation of hexanuclear μ-oxo titanium(IV) alkoxo carboxylato complexes of the general formula $[Ti_6O_6(OR)_6(OOC^tBu)_6]$. Thermal decomposition pathways of these compounds and their potential application in the preparation of TiO_2 nanolayers using chemical vapor deposition (CVD) methods have been discussed. The type of the alkoxide ligands causes differences in the thermolysis pathway, and the type of the volatile decomposition products. Among the examined complexes only $[Ti_6O_6(OR)_6(OOC^tBu)_6]$ (R = ^{i}Bu, $SiMe_3$) show promising properties for their application as precursors in CVD methods. The TiO_2 films were grown in a wide range of substrate temperatures (653–873 °K), under the total reactor pressure 2.0–3.0 mbar. The crystallinity and the composition of layers were analyzed by X-ray diffraction (XRD). It was found that the formation of TiO_2 amorphous, anatase or rutile films depends on the deposition temperature and gas phase composition.

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1. Introduction

The deposition of thin titanium dioxide nanolayers is one of the most extensively studied problems due to its various applications in microelectronics [1–4], optics [5–7], and coatings technologies [8]. Among the methods of deposition used to prepare nanomaterials [9], chemical vapor deposition (CVD) is the most applicable technique for the deposition of thin metal oxide layers. The CVD methodology offers a potential large area of growth, good microstructure and stoichiometric control. The search for the suitable titanium dioxide precursors is the main problem associated with the development of this method. The properties of Ti(IV) compounds that have been most frequently used in CVD are listed in Table 1.

Titanium(IV) alkoxides ($Ti(OR)_4$, R = CH_3, ^{i}Pr, ^{t}Bu) are often applied as TiO_2 precursors in CVD techniques for the preparation of titanium-oxide ceramics, TiO_2 nanoparticle layers and organic–inorganic hybrid polymers [15,16,23–25,9]. The high reactivity of these compounds towards hydrolysis limits their shelf-life, makes them difficult to handle and causes the rapid precipitation of oxo-polymers. Substitution of titanium alkoxides by bidendate ligands, such as carboxylates, leads to the formation of multinuclear μ-oxo titanium(IV) alkoxo carboxylato complexes of reactivity lower than the parent alkoxides [19,21,22,26,27]. An interesting group of compounds are complexes of the general formula $[Ti_6O_6(O^iPr)_6(OOCR)_6]$ (R = ^{t}Bu, $CH_2{}^tBu$) and $[Ti_6O_6(OSiMe_3)_6(OOC^tBu)_6]$, with promising thermal properties for CVD methods. The synthesis, crystal structure and thermolysis pathway of these complexes have been discussed in our earlier papers [28–30]. In comparison to titanium(IV) alkoxides ($Ti(OR)_4$, R = CH_3, ^{i}Pr, ^{t}Bu), the $[Ti_6O_6(O^iPr)_6(OOCR)_6]$ complexes have shown lower reactivity towards hydrolysis and higher thermal stability. Analysis of VT IR and MS data proved the partial decomposition of the studied compounds and the formation of volatile titanium-alkoxide/siloxide species (e.g. $[Ti(OR)_4]$, $[OTi(OR)_2]$) [31]. The further decomposition of these species on the substrate surface leads to the formation of titanium dioxide layers, with the structure depending on the deposition temperature [29]. The previous research proved promising properties of $[Ti_6O_6(O^iPr)_6(OOCR')_6]$ (R′ = ^{t}Bu, $CH_2{}^tBu$) as CVD precursors [29,31]. However, the relatively high decomposition temperatures of the above mentioned complexes caused our interest in the preparation of Ti(IV) compounds which form a similar type of structure and possess thermal properties better than those of $[Ti_6O_6(OPr^i)_6(OOCBu^t)_6]$. Therefore, detailed studies on the thermal decomposition pathway of $[Ti_6O_6(OR)_6(OOCBu^t)_6]$ (R = ^{n}Bu, ^{i}Bu, $Si(CH_3)_3$) have been carried out. In this paper, the influence of the type of alkoxide ligands on the thermal properties of hexanuclear μ-oxo Ti(IV) alkoxo carboxylato complexes and their potential application as TiO_2 precursors in CVD experiments are discussed.

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Table 1
Compounds, which are usually used as TiO_2 precursors in CVD/ALD methods.

Precursor	Method	Deposition temperature, T_D (K)	Allotropic form	Refs.
$TiCl_4$	CVD, ALD	903	Anatase	[10]
TiI_4	CVD	548–983	Amorphous	[11]
	ALD	548–763	Anatase–rutile	[12]
$Ti(NO_3)_4$	CVD	603–1173	Anatase–rutile	[13,14]
$Ti(OCH_3)_4$	ALD	473–673	Amorphous–anatase	[15]
$Ti(O^iPr)_4$	MOCVD-	573–973	Anatase	[9,16]
	Annealing of anatase form	1173	Rutile	
	MOCVD			
	ECR LPMOCVD	773–1023	Rutile	[17]
		293–623	Anatase	[18]
		423–1173	Anatase–rutile	
$Ti(O^tBu)_4$	MOCVD	873	Anatase	[19]
[Ti(μ-ONep)(ONep)$_3$]$_2$	MOCVD	573	Anatase	[20]
[Ti(dpm)$_2$(O^{i}Pr)$_2$]	MOCVD	403–773	Anatase	[21]
[Ti(mpd)(mdop)(μ-OCH)]$_2$	MOCVD	648–723	no data	[22]

mpd – 2-methyl-2,4-pentanediolate; mdop – 4,4-dimethyl-3-oxopentanoate; dpm – 2,2,6,6-tetramethyl-3,5-heptanedionate. ONep – neo-pentoxide.

2. Results and discussion

Hexanuclear μ-oxo Ti(IV) alkoxo carboxylato complexes of the general formula [$Ti_6O_6(OR)_6(OOC^tBu)_6$] have been synthesized in the 1:1 reaction of titanium(IV) alkoxide/siloxide ($Ti(OR)_4$; R = ^{n}Bu, ^{i}Bu, $SiMe_3$) with 2,2-dimethylpropionic acid. The reactions proceed at room temperature and under an inert atmosphere (Ar). Slow evaporation of the reaction mixtures in a glassbox, over 4–8 days lead to the separation of colorless crystalline powders and small single crystals. Analysis of X-ray data, collected at 293 K, exhibited that both [$Ti_6O_6(O^nBu)_6(OOC^tBu)_6$] and [$Ti_6O_6(O^iBu)_6$-$(OOC^tBu)_6$] crystallized in the triclinic space group $P\bar{1}$ (no. 2). The poor quality of the [$Ti_6O_6(O^iBu)_6(OOC^tBu)_6$] crystals (in spite of the multiple preparation experiments) meant that very weak diffraction of the monocrystal was observed. Therefore, a detailed structure of this complex is not reported. Table 2 lists details of the X-ray data collection for the [$Ti_6O_6(O^nBu)_6(OOC^tBu)_6$] complex. Selected bond distances and angels of the studied [$Ti_6O_6(O^nBu)_6$-$(OOC^tBu)_6$] complex are presented in Table 3.

Similarly to the complexes described in our previous papers [28,30], the structures of the investigated compounds consist of hexanuclear titanium μ-oxo cores ([Ti_6-(μ_3-O)$_6$]) and the coordination sphere is completed by carboxylate bridges and terminal alkoxide ligands (Fig. 1). Six equivalent titanium atoms are arranged in the corners of an octahedron. Each titanium atom (coordination number 6) is surrounded by six oxygen atoms (three oxygen atoms of μ_3-O bridges, two of *syn–syn* carboxylate bridges and an oxygen atom of the terminal alkoxide ligand). Analysis of the structural data reveals that the [$Ti_6O_6(O^nBu)_6(OOC^tBu)_6$] complex molecule has C_i symmetry. Therefore half of the molecules with three Ti

Table 2
Details of the crystallographic data collection and the structure refinement for the studied compound.

Crystal data	[$Ti_6O_6(O^nBu)_6(OOC^tBu)_6$]
Formula sum	$Ti_6O_{24}C_{54}H_{108}$
Formula weight	1418.72
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
Unit cell dimensions	
a (Å)	10.1789(2)
b (Å)	14.6566(3)
c (Å)	15.7865(3)
α (°)	114.34(3)
β (°)	101.62(3)
γ (°)	98.20(3)
Cell volume (Å^3)	2020.2(7)
Density (calculated) (Mg/m^3)	1.166
Z	1
Absorption coefficient (mm^{-1})	0.625
F(0 0 0)	746
Crystal size (mm)	0.26 × 0.22 × 0.10
θ Range for data collection (°)	2.68–26.50
Index ranges	$-13 \leqslant h \leqslant 13$
	$-18 \leqslant k \leqslant 18$
	$-15 \leqslant l \leqslant 19$
Reflections collected	15 583
Reflections unique/R_{int}	8346/0.0746
Transmission maximum/minimum	0.9387/0.8539
Data/restraints/parameters	8346/720/473
Goodness-of-fit on F^2	0.955
Final R indices [I > 2σ(I)]	R_1 = 0.0868, wR_2 = 0.2108
R indices (all data)	R_1 = 0.1929, wR_2 = 0.2754
Largest difference in peak and hole [e Å^{-3}]	0.626 and −0.328

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
$WR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w|F_o|^2)^2]^{1/2}$.

Table 3
Selected bond lengths (Å) and angles (°) for the [$Ti_6O_6(O^nBu)_6(OOC^tBu)_6$] complex.

Distances (Å)	
Ti–(μ_3-O)	
Ti1–O1	2.164(4)
Ti1–O2	1.905(4)
Ti1–O3#1	1.888(4)
Ti2–O2	2.163(4)
Ti2–O1	1.898(4)
Ti2–O3	1.894(4)
Ti3–O3	2.130(4)
Ti3–O1#1	1.879(4)
Ti3–O2	1.886(4)
Ti–OR	
Ti1–O10	1.762(4)
Ti2–O11	1.731(5)
Ti3–O12	1.770(4)
Ti–OCO	
Ti1–O4	2.048(5)
Ti1–O8	2.051(4)
Ti2–O6	2.042(5)
Ti2–O5	2.062(5)
Ti3–O7	2.053(5)
Ti3–O9#1	2.054(5)
Angles (°)	
O–Ti–O	
O3#1–Ti1–O2	101.91(2)
O3#1–Ti1–O1	77.01(2)
O2–Ti1–O1	77.20(2)
O3–Ti2–O1	102.00(2)
O3–Ti2–O2	77.60(2)
O1–Ti2–O2	77.40(2)
O1#1–Ti3–O2	102.21(2)
O1#1–Ti3–O3	78.10(2)
O2–Ti3–O3	78.60(2)

Symmetry operation #1: $-x + 1$, $-y + 1$, $-z$.
μ_3-O: O1, O2, O3/OOC: O4, O5, O6, O7, O8, O9/OR: O10, O11, O12.

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