



## Ethyl acetoacetate ligand distribution in the course of titanium *n*-butoxide chelation



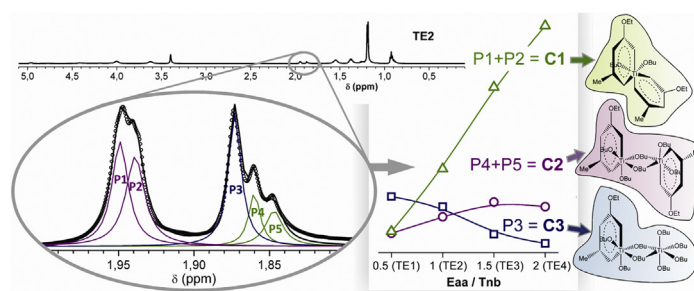
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### HIGHLIGHTS

- Titanium *n*-butoxide was modified with ethyl acetoacetate in various ratios.
- Among other chelate phases, previously undescribed  $Ti_2(O^iBu)_7Eaa$  was obtained.
- NMR-based mass balance procedure was introduced to obtain quantitative relationships.
- The transesterification reaction has been noted.
- Nanocrystalline anatase has been obtained by thermal treatment at 350 °C.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Sols obtained by chelation of titanium *n*-butoxide with ethyl acetoacetate, Eaa, in various ratios have been subjected to FTIR,  $^1H$  and  $^{13}C$  NMR, HSQC and UV–Vis spectroscopy in order to provide insight in the compounds obtained, their structure and quantitative relationships. Three compounds, the bis-chelated monomer,  $Ti(O^iBu)_2(Eaa)_2$ , bis-chelated dimer,  $(Ti(O^iBu)_3Eaa)_2$  and monochelated dimer,  $Ti_2(O^iBu)_7Eaa$  have been established. As the molar ratio Eaa/ $Ti(O^iBu)_4$  increases, the coordination changes from the monochelated and bis-chelated dimer to the bis-chelated monomer. Additionally, the transesterification reaction, influencing the chemical composition of the compounds was noted. The hydrolysis of the prepared sols was partial, leaving some residual butoxy and ethyl acetoacetate groups attached to titanium. Thermal treatment of the prepared amorphous gels at 350 °C yielded with the formation of nanocrystalline anatase. It was noted that high Eaa/Tnb ratio slightly retards the anatase formation.

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### 1. Introduction

Nanocrystalline titania powders have been widely studied in regard to the potential photovoltaic, photocatalytic and optical applications. A good review article on synthesis, properties,

modifications and applications of titanium dioxide nanomaterials has been published by Chen and Mao [1]. The sol–gel process has been extensively used in the preparation of nanocrystalline titania. This process usually involves the use of titanium alkoxides as precursors. The key steps of the sol–gel process are the hydrolysis and condensation of precursors. In order to obtain a material with the aimed properties, the control of those processes is essential. Due to the electronegativity of the alkoxy groups, which makes the metal atoms highly sensitive to nucleophilic attack, alkoxides are

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usually a very reactive species [2]. Therefore, Ti-alkoxides can be very sensitive to water, i.e. prone to rapid hydrolysis making the sol–gel process difficult to control. The chemical modification provides a higher coordination number and steric hindrance yielding with the increased stability of the precursors and enables better control of the hydrolysis and condensation steps [3].

Various chelating agents can be used for the chemical modification of metal alkoxides. Due to their availability and low cost,  $\beta$ -diketones and  $\beta$ -ketoesters are most commonly used [4–7].  $\beta$ -diketones and  $\beta$ -ketoesters are bidentate monocharged ligands, their coordination to the titania centre results in the formation of complexes where both oxygen atoms bind to metal. One less commonly used  $\beta$ -ketoester [5,8], is ethyl acetoacetate ( $C_6H_{10}O_3$ , Eaa). Eaa is capable of undergoing keto–enol tautomerism. The reaction is shown in Fig. 1. If Eaa is pure, the ketonic form predominates while in the presence of Ti alkoxides, the reactive enolic form of Eaa substitutes the alkoxy groups of alkoxide (Fig. 1). A replacement of the reactive alkoxy group with a less hydrolysable entity, i.e., the formation of a six-membered chelate ring, strongly shifts the keto–enolic equilibrium towards the enolic form stabilized by chelation with alkoxide.

Upon chelation, the coordination number of titanium increases. Besides reducing titanium accessibility to nucleophilic attack by water, the chelation also affects the degree of oligomerization. The structure of modified alkoxide further affects the properties of gel formed upon hydrolysis, which is reflected in the physical properties of the final material. Hence, detailed knowledge of the structure of titanium alkoxide precursors modified by chelating agents is of special interest. A better understanding of the chelation process, i.e. the ligand distribution yielding various compounds, would enable better control of the sol–gel process and thus the improvement of the properties of sol–gel derived titania-based materials.

Studies on the modification of various titanium alkoxides with various chelating agents have been reported. Structures of titanium  $\beta$ -diketonate and  $\beta$ -ketoester complexes were first isolated by Yamamoto and Kambara [9], a wide range of alkoxide derivatives were prepared later, a book providing deeper insight in alkoxy and aryloxy derivatives of metals has been published recently [10]. However, the titanium n-butoxide/ethyl acetoacetate system has been less investigated, especially in a systematic manner. For this reasons, in the present study sols obtained by chelation of titanium n-butoxide ( $Ti(OC_4H_9)_4$ , Tnb) with Eaa in various ratios have been subjected to  $^1H$  and  $^{13}C$  NMR investigation. The compounds obtained, their structure and their quantitative relationships have been reported.

## 2. Experimental

### 2.1. Synthesis

The sols were prepared using titanium n-butoxide, Tnb ( $Ti(O^iBu)_4$ , 98%, Alfa Aesar, Germany) and ethyl acetoacetate, Eaa

( $C_6H_{10}O_3$ , 98%, Fluka, Germany) while 2-propanol ( $C_3H_7OH$ , 99%, Kemika, Croatia) was used as a solvent. All chemicals were used as received. Four sols were prepared, with Eaa/Tnb molar ratios of 0.5, 1, 1.5 and 2, denoted TE1, TE2, TE3 and TE4, respectively. Such ratios were selected bearing in mind that titanium is preferentially six coordinated so the Eaa/Tnb ratios higher than 2 would yield no further expansion of the coordination sphere.

The appropriate amount of Eaa (0.05, 0.1, 0.15 and 0.2 mol) was firstly added to the 0.5 mol of solvent and then 0.1 mol of Tnb was dissolved in the solvent/Eaa solution. Tnb was added to the solution using a syringe to minimize exposure to air humidity. When Tnb was added to the Eaa/solvent solution the exothermic process occurred. The mixture was stirred in a closed reactor for 24 h at room temperature, no precipitation was observed. Sols were stored in a closed container for further analysis.

The clear sols were poured into large Petri dishes in order to maximize exposure to air moisture and kept at room temperature until gellation. Drying of the samples for five more days at room temperature enabled the evaporation of solvent. The obtained samples were subsequently grinded to fine powders and stored.

### 2.2. Characterization

The IR spectra of the samples were acquired using the Fourier transform infrared spectrometer Bruker Vertex 70 in ATR (attenuated total reflectance) mode. The samples were deposited on a diamond and the absorbance data was collected between 400 and 4000  $cm^{-1}$  with a spectral resolution of 1  $cm^{-1}$  and average of 64 scans. The UV–Vis spectra were measured on a Varian UV/VIS Cary 50 spectrophotometer.

$^1H$  and  $^{13}C$  NMR spectra of sols were recorded in high-resolution NMR Spectrometer Bruker Avance 300, operating at 300 MHz for  $^1H$  resonance and for  $^{13}C$  at 75 MHz. The Heteronuclear Single Quantum Coherence spectra (HSQC) were recorded at 600 and 150 MHz for  $^1H$  and  $^{13}C$  NMR spectra, respectively. The samples were dissolved in  $CDCl_3$  containing tetramethylsilane as the internal standard and measured in 5 mm NMR tubes. The  $^1H$  and  $^{13}C$  NMR chemical shift values ( $\delta$ ) are expressed in ppm referring to tetramethylsilane. The NMR peak assignments of various titanium complexes obtained from different molar ratios were analyzed in details using one- and two-dimensional  $^1H$  and  $^{13}C$  NMR spectroscopy. Assignments of  $^1H$  and  $^{13}C$  NMR spectra were performed on the basis of chemical shifts, signal intensities, magnitude and multiplicity of H–H coupling constants, literature references and according to the NMR spectra of the pure samples of Eaa,  $Ti(O^iBu)_4$ , and 2-propanol. The deconvolutions of the spectra were accomplished by fitting the peaks to the Lorentz function.

The powder crystal X-ray diffraction (XRD) was accomplished using Shimadzu diffractometer XRD 6000 with  $CuK\alpha$  radiation. Data were collected between 10 and 60°  $2\theta$  and 10–80°  $2\theta$  for raw and thermally treated gels, respectively, in a step scan mode with

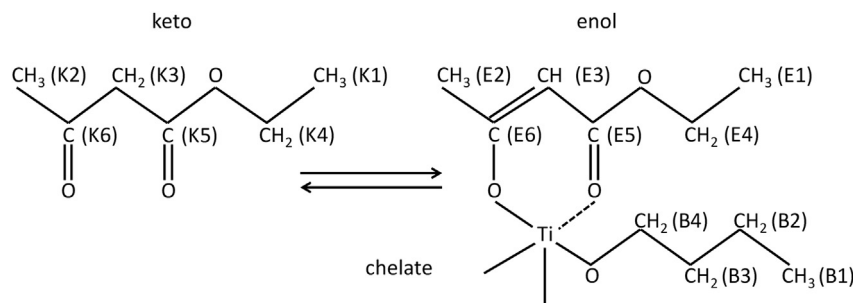


Fig. 1. Keto–enol tautomerism and the formation of chelate. Notations are introduced for the interpretation of  $^1H$  and  $^{13}C$  NMR signals.

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