Journal of Thermal Analysis and Calorimetry, Vol. 75 (2004) 25–34

PYROLYSIS STUDY OF SOL–GEL DERIVED TiO_2 POWDERS

Part IV. TiO_2-anatase prepared by hydrolysing titanium(IV) isopropoxide without chelating agents

R. Campostrini [1*], *M. Ischia* [1] *and L. Palmisano* [2]

[1]Dipartimento di Ingegneria dei Materiali, Università di Trento, via Mesiano 77, 38050 Trento, Italy
[2]Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo,
Viale delle Scienze, 90128 Palermo, Italy

(Received March 27, 2003; in revised form September 25, 2003)

Abstract

An amorphous TiO_2 gel was obtained by hydrolysing titanium(IV) isopropoxide with a stoichiometric amount of water using $SnCl_2$ as catalyst. In these operative conditions, a TiO_2 gel matrix containing a lower fraction of organic residual was obtained with respect to samples prepared by previously modifying the titanium alkoxide precursor with chelating ligands. Dried gel powders were characterized by N_2 adsorption analyses, FT-IR and XRD measurements. Thermogravimetric (TG) and differential thermal analysis (DTA) coupled with mass spectrometric (MS) and gas chromatographic (GC) measurements were performed in order to identify the organic products released from TiO_2 gel pyrolysis. The TG-MS semiquantitative analysis of the main evolved species allowed to describe both the chemical composition of the initial TiO_2 gel and the chemical rearrangements occurring in the matrix during heating up to its crystallisation to anatase form at 420°C.

Keywords: pyrolysis study, thermogravimetric-mass spectrometric coupled analyses, TiO_2 gel

Introduction

As previously reported, our interest is the sol–gel preparation of polycrystalline TiO_2 anatase powders to be employed as catalysts in photo-oxidation processes for pollutants degradation present in diluted wastewater [1–6]. The versatility of the sol–gel method allows the preparation of amorphous TiO_2 gels with tailored morphological properties such as, for instance, high specific surface areas [7]. This feature can be achieved if the hydrolysis of Ti precursor units is properly addressed towards a linear growth of the Ti–O–Ti polymer chains by means of an acidic catalysis in the presence of HCl and the modification of the alkoxide titanium precursor into less reactive oligomeric units [8, 9].

---

[*] Author for correspondence: E-mail: renzo.campostrini@ing.unitn.it

1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

To this aim, we studied the effect of different chelating ligands on titanium(IV) isopropoxide precursor in preparing amorphous TiO_2 matrices, for which a subsequent thermal treatment was required to crystallize the TiO_2 network to anatase form obtaining active materials for photocatalytic applications [10–12]. Undesirably, the modification of Ti precursor by means of stabilizing ligands increases the organic content remaining into the TiO_2 matrices. Consequently, a more prolonged thermal treatment of these samples is required for their 'inorganication' into a pure TiO_2 structure in order to improve the catalytic performances. On the other hand, any thermal treatment leads to collapse of the initial specific surface area of the gel and/or enlargement of the TiO_2-anatase crystallite sizes, reducing the catalytic properties. These phenomena are due to the occurrence of reactions inside the TiO_2 network induced at definite temperatures and times. For these reasons, some attempts were made to find new catalytic conditions for a direct hydrolysis carried out on pure titanium alkoxides, avoiding the use of chelating agents.

In this work we report the preparation and the pyrolysis study of a TiO_2 gel obtained by hydrolyzing titanium(IV) isopropoxide with water in the presence of catalytic amounts of $SnCl_2$. The formation of labile unsaturated Sn(II) alkoxyl complexes seems to mediate the water molecules attack to titanium alkoxide species, quenching their initial reactivity, although the effective role of Sn^{++} ions in the hydrolysis mechanism is not completely ascertained. The chemical composition of the gel, obtained by this alternative catalytic condition and characterized by a remarkable high surface area and low residual organic content, was deduced from the well-tested TG-MS/TG-GC-MS data processing. Moreover, the easy elimination of the lower organic content from this TiO_2 gel matrix requires a mild thermal treatment for the TiO_2-anatase crystallization. This heating at lower temperatures affords powders characterized by TiO_2 polycrystallites of smaller sizes and higher surface hydroxyl groups density, yielding materials with potential enhanced catalytic properties [13–15].

Experimental procedure

Chemicals and instrumentation

Titanium isopropoxide (98.5%) was purchased from ABCR, tin(II) chloride dihydrate (98%) and 2-propanol (99%) were Aldrich reagent grade products. All chemicals were used as received without any further purification.

Details on instrumentation and analysis procedures used to characterise the TiO_2 samples are reported in part 1 [10].

Synthesis of sample

24.0 cm^3 of 2-PrOH (0.313 mol) were used to dilute 9.33 cm^3 of $Ti(OCH(CH_3)_2)_4$ ($3.13\cdot10^{-2}$ mol) working under nitrogen flow, then 35.3 mg of $SnCl_2\cdot2H_2O$ ($1.56\cdot10^{-4}$ mol) were added yielding a pale yellow solution. The alkoxide precursor was hydrolyzed by adding dropwise a solution of 0.58 cm^3 of distilled water ($3.13\cdot10^{-2}$ mol) diluted in

24.0 cm^3 of 2-PrOH (0.313 mol). The reacting emulsion was kept under vigorous stirring for 4 days up to gelling. Sol–gel parameters were Ti-alkoxide (precursor):2-propanol (solvent):water:$SnCl_2$ (hydrolysis catalyst)=1:20:1:0.005. The yellow transparent wet gel was aged in air for one week. The solid sample was then milled to fine powders, dried at room temperature for 4 days and under vacuum (10^{-2} hPa) for further 2 days, yielding the xerogel sample used in the characterization study. This titania sample was labelled: TiO_2–Sn.

Results and discussion

Specific surface area and porosity determinations, FTIR and XRD data

An isotherm curve typical of a mesoporous sample was obtained in the nitrogen adsorption measurements carried out on the TiO_2–Sn gel. A specific surface area of 380 m^2 g^{-1} and an average pore diameter value of 2.4 nm were calculated from adsorption data by B.E.T. and B.J.H. equations [16, 17].

Infrared spectrum of TiO_2–Sn gel shows two intense broad bands centred at 3350, 1628 and 600 cm^{-1} respectively, due to –O–H and ≡Ti–O–Ti≡ absorptions [18]. Very weak signals at 2970, 1463, 1379 and 1130 cm^{-1} attributable to residual alkoxide groups are present in the crude gel [19, 20]. These last absorptions drastically decreased in samples heated above 350°C and totally disappeared in samples treated up to 450°C, as shown in Fig. 1.

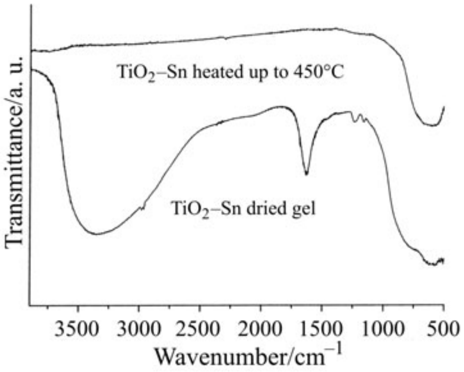

Fig. 1 FT-IR spectra of TiO_2–Sn sample dried at room temperature and after heat treatment up to 450°C

XRD pattern presents a broad band for the crude gel in agreement with the case of amorphous powders. The typical diffraction peaks of TiO_2-anatase were found for the sample annealed at 450°C according to JCPDS card n° 21-1272, as shown in Fig. 2.

Pyrolysis study

As shown in Fig. 3, thermogravimetric (TG) curve of TiO_2–Sn gel presents a total mass loss of 24.8% intensity in the 60–900°C range, characterized by two events cen-

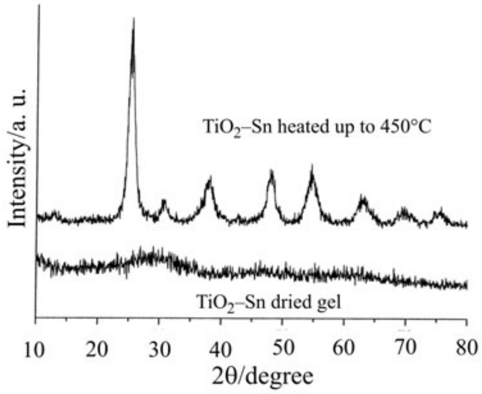

Fig. 2 X-ray diffraction analyses of TiO_2–Sn sample dried at room temperature and after heat treatment up to 450°C

tred at 125 and 220°C, as evidenced in DTG curve. DTA analysis presents an endothermic broad band followed by a smaller shoulder corresponding to the TG events, and an exothermic intense sharp peak at 420°C [21].

Total ion curve (*TIC*) (Fig. 3) is characterized by two partially overlapped bands in the range 60–350°C: the former centred at 130°C, the latter, more intense, at 225°C.

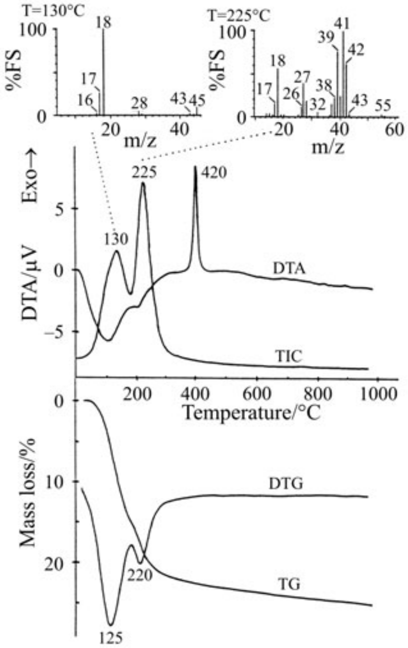

Fig. 3 Thermogravimetric mass spectrometric coupled analysis of TiO_2–Sn gel. TG, DTG, DTA curves with the total ion curve (*TIC*) plot of the evolved gas phase *vs.* pyrolysis temperature. In the insets mass spectra recorded at the maximum of the *TIC* peaks

Mass spectra recorded for temperatures related to the first *TIC* peak indicate the release of H_2O (Fig. 3, inset T=130°C, *m/z* signals at 18, 17, 16), whereas for the second *TIC* peak the main evolution of $CH_3CH{=}CH_2$ (T=225°C, *m/z* 42, 41, 39) with minor amount of H_2O is observed.

TG-GC-MS analyses, with injections carried out at 125 and 220°C, give gas chromatographic elutions which confirm the presence of these species and show smaller amount of 2-PrOH during the first mass loss, as shown in Fig. 4.

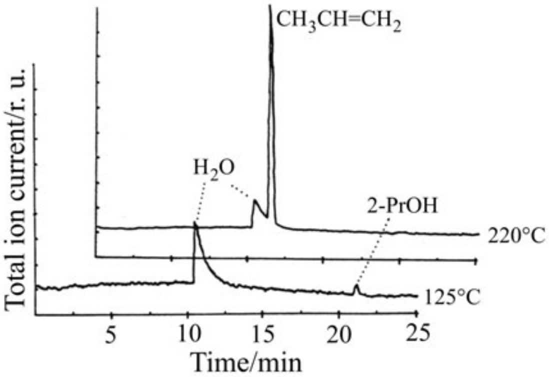

Fig. 4 Gas chromatographic elutions (PoraplotQ column) of the gas phase evolved at 125 and 220°C in the pyrolysis of TiO_2–Sn gel

As previously reported [10–12], the release of some gaseous species during the pyrolysis process can be easily followed from the trend of appropriate *m/z* ion currents, recalled from TG-MS data analysis. The first evolved species is 2-propanol, detected by its most intense fragmentation ion $[CH_3CHOH]^+$. Actually, its *m/z* 45 ion current, showed in Fig. 5, gives rise to the small band centred at 100°C. At these temperatures 2-propanol arises both from adsorbed molecules and thermally activated condensation reactions between vicinal isopropoxide and hydroxyl groups present inside the TiO_2 network:

$$\equiv\mathrm{Ti{-}OH}+(\mathrm{CH_3})_2\mathrm{CH{-}O{-}Ti}\equiv\rightarrow\equiv\mathrm{Ti{-}O{-}Ti}\equiv+(\mathrm{CH_3})_2\mathrm{CHOH}(g) \tag{1}$$

The second released species is H_2O, monitored by its molecular ion (*m/z*=18), giving rise to a current ion which is characterized by an asymmetrical band centred at 130°C and a small tail up to 250°C. Similarly to the alcohol, water can derive both from physically entrapped molecules and the condensation reaction between residual hydroxyl groups:

$$\equiv\mathrm{Ti{-}OH}+\mathrm{HO{-}Ti}\equiv\rightarrow\equiv\mathrm{Ti{-}O{-}Ti}\equiv+\mathrm{H_2O}(g). \tag{2}$$

At higher temperatures, the consumption of the last residual isopropoxide groups, still present inside the TiO_2 network, occurs by elimination reaction with propene evolution:

$$\equiv\text{Ti–OCH(CH}_3)_2\rightarrow\equiv\text{Ti–OH+CH}_3\text{–CH=CH}_2(g). \quad (3)$$

This unsaturated hydrocarbon, monitored by its more intense fragmentation ions $[CH_2CHCH_2]^+$, leads to a *m/z* 41 ion curve presenting a sharp band centred at 225°C.

The pyrolysis process of this TiO_2–Sn sample appears quite simple in comparison with those of gels obtained from ligand-modified titanium alkoxides, being 2-propanol, propene and water the only detected species. Indeed, the complete description of the pyrolysis is confirmed by the perfect overlap observed between the total ion current curve and the curve obtained from the sum of the ion currents (Σ*m/z*) selected to monitor the release of these three chemical species, as shown in Fig 5.

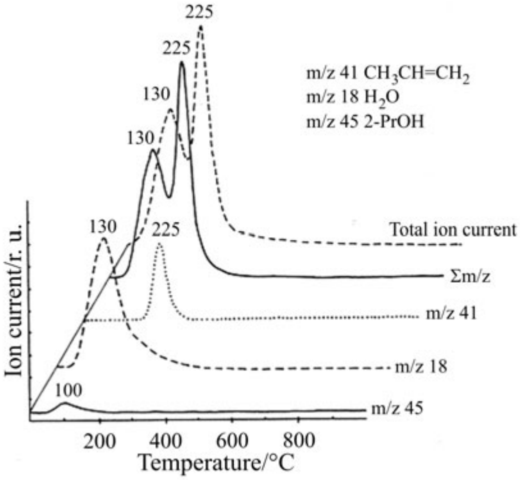

Fig. 5 Ion currents of selected ions used to represent the release of evolved species during TiO_2–Sn gel pyrolysis. The intensity of these *m/z* ion currents are plotted taking into account the molecular ratio values found for the species in the semiquantitative gas phase analysis during the whole pyrolysis process (Table 2). Comparison between the sum of these ion currents (Σ*m/z*) curve and the total ion current (*TIC*) one

A semiquantitative evaluation of pyrolysis data

The TG-MS analysis was carried out on 33.2 mg of TiO_2–Sn sample, yielding at 1000°C 25.0 mg of residual solid, assumed to be a pure TiO_2 matrix, and 8.2 mg of evolved gas phase composed only by a mixture of 2-PrOH, propene and H_2O. As presented in [10], the released amounts of these compounds are quantified by processing the TG-MS analysis data. Table 1 summarizes the relative intensities of all ions (*i*) present in the mass spectrum of the pure substance (*j*), as recorded in the TG-GC-MS gas chromatographic elutions, in addition to the integrated values of the selected *m/z* ion currents ($Im/z(i)_j$), extrapolated from the TG-MS data, used to quantify the amount of the evolved gas species.

Released H_2O and 2-PrOH were directly calculated starting from the integrated values of their representative ions

Table 1 Data from mass spectra of pure chemical species (recorded in TG-GC-MS measurements) and from integrated values of *m/z* ion currents (recorded in TG-MS measurement)

Chemical species, representative ion [integrated *m/z* value obtained by TG-MS analysis/a. u.]	*m/z* ions from mass spectra of pure substances in TG-GC-MS analyses; (peak height/mm) [integrated *m/z* signal value/a. u.][a]	Sum of the peak heights/mm [integrated amount value of the chemical species, a. u.]
H_2O, 18 [$208.55\cdot10^6$]	16(1); 17(19); 18(88) [$208.55\cdot 10^6$]	108 [$255.94\cdot10^6$]
2-Propanol, 45 [$3.64\cdot10^6$]	15(4); 16(1); 19(6); 27(19); 28(6); 29(13); 31(7); 32(3); 39(6); 40(3); 41(8) [$0.33\cdot 10^6$]; 42(3); 43(18); 44(5); 45(88) [$3.64\cdot 10^6$]; 59(4)	94 [$8.03\cdot10^6$]
Propene, 41 [$45.28\cdot10^6$]	14(1); 15(2); 19(2); 20(2); 26(5); 27(19); 36(2); 37(12); 38(17); 39(61); 40(23); 41(88) [$44.95\cdot 10^6$]; 42(54); 43(2)	294 [$150.16\cdot10^6$]

[a] For the sake of conciseness, only the values used in the processing data are summarized.

$$Im/z(18)_{\text{water}}=208.5510^{6} \text{ and } Im/z(45)_{\text{2-propanol}}=3.64\cdot 10^{6}.$$

Subsequently, the amount of the evolved propene was calculated by considering the value of the integrated signal of *m/z* 41 ion current and by subtracting the contribution arising from 2-propanol:

$$Im/z(41)_{\text{propene}}=Im/z(41)_{\text{TG-MS data}}-Im/z(41)_{\text{2-propanol}}=45.28\cdot 10^{6}-0.33\cdot 10^{6}=44.95\cdot 10^{6}.$$

The absolute amounts of each released species and the chemical composition of the gas phase evolved during the entire pyrolysis are reported in Table 2.

Table 2 Chemical composition of gas mixture (8.2 mg) evolved in the whole TiO_2–Sn pyrolysis process calculated from the TG-MS data

Chemical species (molecular mass)	Molar%	Mass%	Amount/mmol
H_2O (18)	61.8	40.4	0.184
2-Propanol (60)	1.94	4.2	$5.8\cdot 10^{-3}$
Propene (42)	36.3	55.3	0.108

By taking into account these data and the reactions involved in the pyrolysis process (Eqs (1) – (3)), which implies that

$$\equiv\text{Ti–OH groups}= \\ 2(\text{evolved } H_2O \text{ molecules})+(\text{evolved 2-PrOH molecules}) - \\ -(\text{evolved } CH_3CH{=}CH_2 \text{ molecules})$$

and

$$\equiv\text{Ti–OCH}(CH_3)_2 \text{ groups}= \\ (\text{evolved 2-PrOH molecules})+(\text{evolved } CH_3CH{=}CH_2 \text{ molecules}),$$

the absolute residual hydroxyl and isopropoxide groups present in the starting TiO_2–Sn gel can be easily calculated. Consequently, by considering the 0.313 mmol of Ti atoms content in the pyrolyzed residual solid, 0.266 mmol of ≡Ti–OH groups and 0.114 mmol of ≡Ti–$OCH(CH_3)_2$ moieties were obtained. Finally, from the difference between the number of titanium atom bonds and the number of bonds with terminal groups, the presence of 0.436 mmol of bridging oxygen atoms were deduced.

This chemical composition leads to a nominal mass balance of 33.2 mg, which is exactly the same amount of gel that was treated in the experimental TG-MS measurement. As a matter of fact, the crude TiO_2–Sn gel can be so carefully described by the nominal formula:

$$TiO_{1.39}(OH)_{0.85}(OCH(CH_3)_2)_{0.36}.$$

Conclusions

Titania gels of high specific surface areas (up to 480 $m^2 g^{-1}$ in the case of TiO_2–Fo sample) were easily obtained in these comprehensive works by hydrolysing titanium(IV) isopropoxide under strong acidic catalytic conditions, i.e. by using a HCl solution (pH=0) in stoichiometric molar ratios. Nevertheless, a preliminary modification of the monomeric precursor units (by reaction with suitable chelating agents) was required under these operative conditions in order to control the too high reaction rate of the original titanium alkoxide. On the other hand, gels prepared by using formic, oxalate or acetate ligands presented a high residual organic content due to their incomplete hydrolysis before the gelling process. Moreover, the heat treatments carried out on these organic-modified gels, in order to purify the TiO_2 inorganic matrices, required higher temperatures to crystallize the anatase phase (from 415°C for the TiO_2–Fo sample up to 535°C for the TiO_2–Ox one) with quite intense mass losses (from 32.0% for the TiO_2–Fo up to 45.9% for the TiO_2–Ox).

In this last contribution, the hydrolysis carried out on the pure titanium alkoxide assisted by Sn(II) species catalyst yielded a homogeneous TiO_2 sample with a remarkable specific surface area (380 $m^2 g^{-1}$). The thermal treatment of TiO_2–Sn sample, prepared in the absence of ligand, gave rise to the lowest mass loss (24.7%) and to the occurrence of crystallization at a modest temperature (420°C). Consequently, an exhaustive description of the pyrolysis was possible by coupling thermogravimetric, mass spectrometric, and gas chromatographic analyses because of the low organic content of the TiO_2 matrix (due to the exclusively not-hydrolysed isopropoxide groups). The first chemical rearrangement, occurring in the TiO_2 network during heating, was the condensation reactions between vicinal hydroxyl and isopropoxide groups with release of 2-propanol and water observed at 100 and 130°C, respectively. The easier consumption of the $\equiv$Ti–OH groups led then to a TiO_2 matrix still maintaining residual $\equiv Ti–OCH(CH_3)_2$ moieties; these groups, instable at higher temperatures, underwent a thermal decomposition with propene elimination at 220°C. Moreover, TG-MS data elaboration reported in this last and in the previous contributions [10–12], allowed a quantitative determination of the organic content present into the TiO_2 gel matrices. In particular, for the TiO_2–Sn sample studies in this work the perfect agreement between the experimental data and the mass balance values derived from the TG-MS data elaboration confirms the reliability of the proposed pyrolysis mechanism and provides an acceptable description of the chemical structure of the crude TiO_2 gel.

References

1 D. F. Ollis and H. Al-Ekabi, Photocatalyic Purification and Treatment of Water and Air, Elsevier, Amsterdam 1993.
2 G. R. Helz, R. G. Zepp and D. G. Crosby, Aquatic and Surface Photochemistry, Lewis Publishers, Boca Raton 1994.
3 V. Augugliaro, L. Palmisano, A. Sclafani, C. Minero and E. Pelizzetti, Toxicol. Envir. Chem., 16 (1988) 2015.

4 R. Campostrini, G. Carturan, L. Palmisano, M. Schiavello and A. Sclafani, Mater. Chem. Phys., 38 (1994) 277.

5 G. Marcì, L. Palmisano, A. Sclafani, A. M. Venezia, R. Campostrini, G. Carturan, C. Martin, V. Rives and G. Solana, J. Chem. Soc., Faraday Trans., 92 (1996) 819.

6 G. Facchin, G. Carturan, R. Campostrini, S. Gialanella, L. Lutterotti, L. Armelao, G. Marcì, L. Palmisano and A. Sclafani, J. Sol–Gel Sci. Techn., 18 (2000) 29.

7 C. J. Brincker and G. W. Scherer, Sol–Gel Science, The Physics and Chemistry of Sol–Gel Processing, Ed. Academic Press, San Diego, CA 1990.

8 B. E. Yoldas, J. Mater. Sci., 21 (1986) 1087.

9 Bokhimi, A. Morales, O. Novaro, T. Lopez, E. Sanchez and R. Gomez, J. Mater. Res., 10 (1995) 2788.

10 R. Campostrini, M. Ischia and L. Palmisano, J. Therm. Anal. Cal., 71 (2003) 997.

11 R. Campostrini, M. Ischia and L. Palmisano, J. Therm. Anal. Cal., 71 (2003) 1011.

12 R. Campostrini, M. Ischia and L. Palmisano, submitted to J. Therm. Anal. Cal. 75 (2004) 13.

13 E. Sanchez and T. Lopez, Mater. Lett., 25 (1995) 271.

14 D. Robert and J. V. Weber, J. Mater. Sci. Lett., 18 (1999) 97.

15 W. W. So, S. B. Park and S. J. Moon, J. Mater. Sci. Lett., 17 (1998) 1219.

16 S. J. Gregg and K. S. W. Sing, Adsorption, Surface Area and Porosity, Ed. Academic Press, London 1982.

17 P. A. Webb and C. Orr, Analytical Methods in Fine Particles Technology, Ed. Micromeritics Instrument Corporation, Norcross, USA 1997.

18 T. Lopez, E. Sanchez, P. Bosch, Y. Meas and R. Gomez, Mater. Chem. Phys., 32 (1992) 141.

19 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York 1986.

20 N. B. Colthup, L. H. Daly and S. E. Wiberley, Introduction to Infrared and Raman Spetroscopy, Academic Press, San Diego 1990.

21 B. D. Stojanovic, Z. V. Marinkovic, G. O. Brankovic and E. Fidancevska, J. Therm. Anal. Cal., 60 (2000) 595.