

Investigación

Tetraethylortosilicate and Titanium Tetraisopropoxide as Complexing Agents for Chromium(III) and Copper(II)

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Abstract. Tetraethylortosilicate and titanium tetraisopropoxide, two of the most widely used agents in the sol-gel technique, are employed as ligands for chromium(III) and copper(II). Thermal stability of the obtained compounds is studied through thermogravimetric analysis and the products of their pyrolysis through powder X Ray Spectroscopy, scanning electron microscopy and energy dispersive spectrometry. These products are potential precursors for metallic oxide composites.

Key words. Chromium(III), copper(II), Tetraethylortosilicate, titanium tetraisopropoxide, complexes, metallic oxide composites.

Resumen. Tetraetilortosilicato y tetraisopropóxido de titanio, dos de los agentes más comunes en la química Sol-Gel, son usados como ligandos de cromo(III) y cobre(II). Se estudia la estabilidad térmica de los compuestos obtenidos mediante análisis termogravimétricos y los productos de pirólisis se analizan por espectroscopía de rayos X en polvo, microscopía electrónica de barrido y espectroscopía por dispersión de energía. Los compuestos constituyen potenciales precursores de materiales compuestos ("composites") de óxidos metálicos.

Palabras clave: cromo(III), cobre(II), Tetraetilortosilicato, tetraisopropóxido de titanio, complejos, materiales compuestos de óxidos metálicos.

Introduction

Research in Materials Science requires of new synthetic routes to produce materials with complex stoichiometry as those found in superconducting ceramics, or with intricate architectures as those of zeolites. These new strategies should control the solid state structures at atomic level, and represent an important advance in Materials Science. A good approach to materials synthesis is to use the so called molecular precursors, which open the possibility of achieving fine control of the stoichiometry with the extra advantage of the process occurring at low temperatures [1-3].

Particular attention has been given to materials based on metallic oxides due to their importance as catalysts, superconductors, ferroelectrics and semiconductors, among others. The technique known as sol-gel is one of the most widely used to obtain oxide materials, using metallic alkoxides as starting materials, through processes of hydrolysis/condensation. The products can be obtained in different forms including films, monoliths, fibers, etc [4-11].

The present work is a study of the chemistry of transition metals with two of the most commonly used alkoxides in the sol-gel technique, *i.e.*: tetraethylortosilicate (TEOS) and titanium tetraisopropoxide (TIPO). These alkoxides were used as ligands for chromium(III) and copper(II), obtaining potential molecular precursors for mixed metal oxides. In addition, the characterization of the pyrolysis products of the synthesized compounds was done.

Results and discussion

Anhydrous metal halides such as CrCl_3 are compounds with a strong tendency to form adducts with electron pair donor ligands. TIPO and TEOS are alkoxides with non bonding electron pairs ready to establish coordinated bonds. The reactions must occur in a non coordinating media to preclude that solvent could compete with either TIPO or TEOS. The change in color during the formation reactions of $\text{CrCl}_3 \cdot \text{Ti}(\text{OiPr})_4$ (**1**) or $\text{CrCl}_3 \cdot \text{Si}(\text{OEt})_4$ (**2**) and the chemical composition of the products are evidence of the coordination of TEOS and TIPO with the chromium(III) ion, without chlorine substitution. Thermogravimetric analysis of compounds **1** and **2** show that thermal decomposition starts at a relatively low temperature: 195 °C and 215 °C respectively (Fig. 1). Compound **1** shows a more pronounced change than **2** at about 200 °C and a second thermal decomposition at 600 °C. These data could be indicative of a weak coordinated bond between TIPO and TEOS and the chromium(III) ion. This conclusion is supported by the fact that when trying to crystallize these compounds in THF, crystals of the well known adduct $\text{CrCl}_3 \cdot 3\text{THF}$ are produced. The boiling points of TEOS (168 °C) and TIPO (232 °C) are similar to the thermal decomposition from compounds (**1**) and (**2**), fact that also supports the conclusions.

Pyrolysis at 500 °C for both compounds under oxygen produces a mixture of oxides. Elemental microanalysis shows the presence of the expected elements: Cr, O, Si and Ti. Fig. 2 is a typical EDS for compound **2**. X Ray diffractograms from the

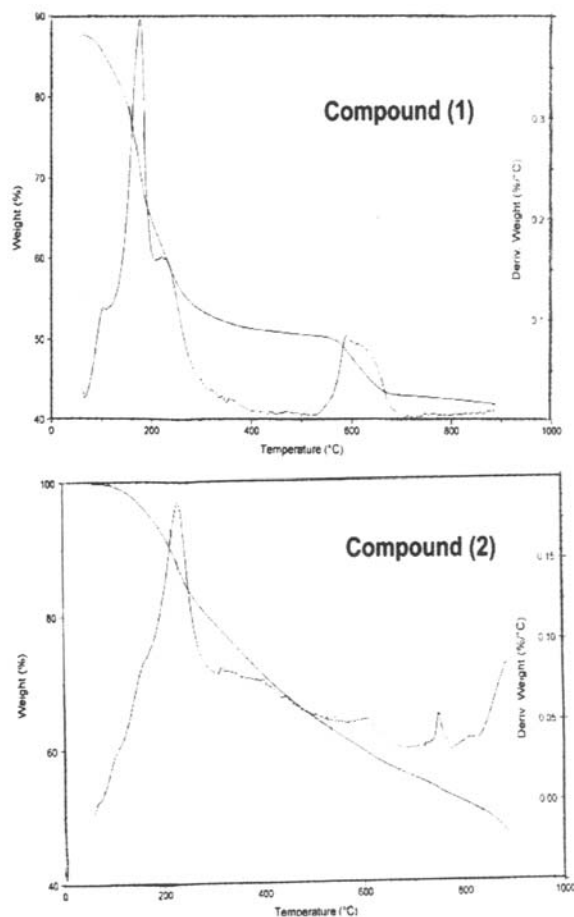


Fig. 1. TGA-DTA for compounds $\text{CrCl}_3 \cdot \text{Ti}(\text{O}i\text{Pr})_4$ (1) and $\text{CrCl}_3 \cdot \text{Si}(\text{OEt})_4$ (2), done under nitrogen with a heating ramp of $10^\circ\text{C min}^{-1}$. Thermal decomposition starts at 195 and 215°C respectively.

pyrolysis solid residue show eskolaite, Cr_2O_3 , as the only crystalline phase (Fig. 3). This fact indicates that both silica and titanium dioxide are amorphous. SEM micrograph from the pyrolysis product from compound 1 shows clusters smaller than $1\ \mu\text{m}$ (Fig. 4), but it is not possible to distinguish crystals from the different oxides, not even at larger magnifications, therefore an interesting composite with very small particles has been prepared.

Electron microscopy (Fig. 5) of a sample corresponding to compound 2 shows crystalline whiskers of Cr_2O_3 up to $6\ \mu\text{m}$ long. These whiskers radiate out of a common origin. The rounded particles were identified with EDS as amorphous silica and have sizes in the order of $4\ \mu\text{m}$. Also in Fig. 5, one can observe regions in which both Cr_2O_3 and SiO_2 are mixed with particles so small that it is not possible to determine their size even at higher magnifications. X-ray diffractograms of these products show the same as that for compound 1, *i.e.*: eskolaite, Cr_2O_3 , as the only crystalline phase. Therefore, no such XRD is included.

The reaction of $\text{CuCl}_2(\text{H}_2\text{O})_2$ with TEOS and TIPO allows to explore the possibility of bonding these ligands with

the water coordinated to the copper atom and its effect on the strength of the bond produced.

Thermogravimetric analysis of the copper compounds $\text{CuCl}_2(\text{OH})_2 \cdot \text{Ti}_2(\text{O}i\text{Pr})_6$ (3) and $\text{CuCl}_2(\text{OH})_2 \cdot \text{Si}_2(\text{OEt})_6$ (4), shows that the thermal decomposition starts at 590°C and 560°C respectively (Fig. 6). There is a clear difference with the thermal decomposition temperatures for the chromium compounds, this is indicative of the greater strength of the copper-ligands bonds. This fact suggests that the presence of water in the coordination sphere of the metal is determinant in the type of product of the reaction, producing partial hydrolysis of the ligand and formation of a bond type $\text{Cu-O-Ti}(\text{Si})$.

The copper compounds were also burnt in oxygen at 500°C . EDS analysis from the products so obtained (not included) show the expected presence of Cu, O, Si, and Ti. The pyrolysis products from compound 3 show the tenorite phase for CuO and the anatase phase for TiO_2 (Fig. 7). SEM electrograph for this solid show CuO crystals between 3 and $10\ \mu\text{m}$ embedded in the TiO_2 matrix (Fig. 8). The X-ray diffractogram (not included) from the pyrolysis product of compound 4 shows only the tenorite phase, thus SiO_2 is amorphous. SEM observation is very similar to the one already described, with crystals up to $10\ \mu\text{m}$ in the SiO_2 matrix.

Experimental

General method

All manipulations were carried out under nitrogen atmosphere, using Schlenk or dry box techniques. Toluene was distilled over sodium under nitrogen. CrCl_3 was prepared according to the literature [12]. The synthesized samples were analyzed with an X Ray powders diffractometer, Siemens D5000 and observed with a scanning electron microscope (SEM), Philips XL-30, equipped with an EDAX energy dispersive spectroscopy probe (EDS). Thermogravimetric analysis were performed in a V2.5H TA Instruments.

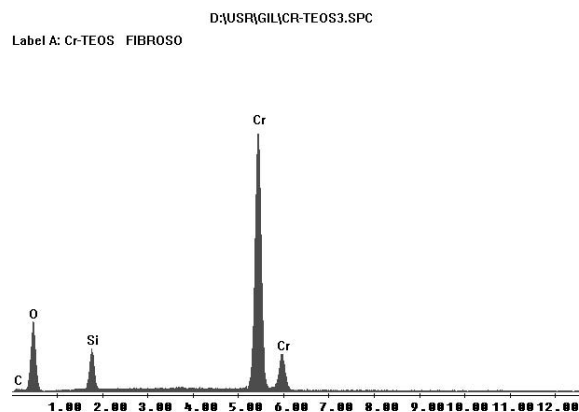


Fig. 2. Typical microanalysis for one sample from the pyrolysis product of compound 2. The presence of Si, O, Cr is observed. Carbon comes from the sample holder.

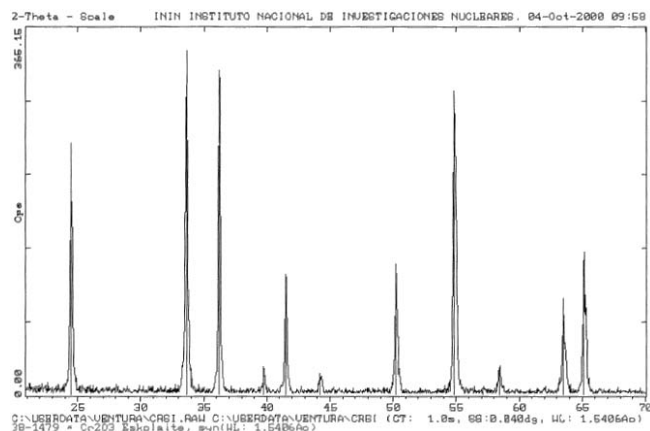


Fig. 3. X Ray diffractogram from the pyrolysis product of CrCl₃·Ti(OiPr)₄ (1). It shows eskolaite Cr₂O₃ as the only crystalline phase present. Diffractogram from the pyrolysis product of compound (2) is identical.

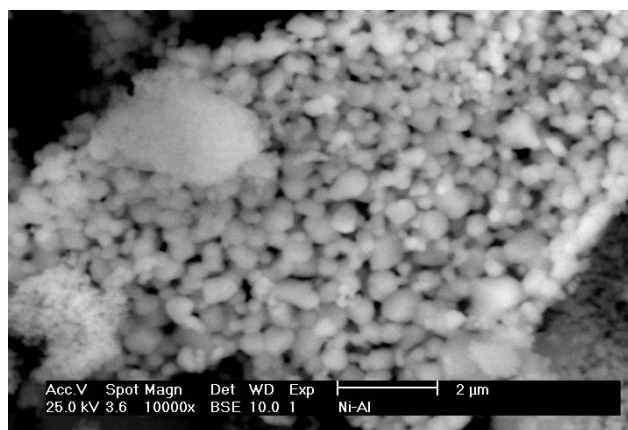


Fig. 4. Electron micrograph from the pyrolysis product of CrCl₃ · Ti(OiPr)₄ (1). Clusters of the composite with sizes under 1 μm.

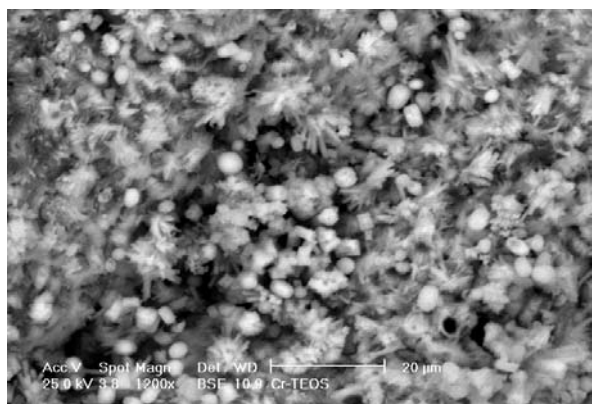


Fig. 5. SEM electrograph from the pyrolysis product of CrCl₃ · Si(OEt)₄ (2). It shows long Cr₂O₃ crystallites up to 6 μm long, in most cases several of these whiskers have a common origin. They are surrounded by amorphous silica particles with sizes in the order of 4 μm.

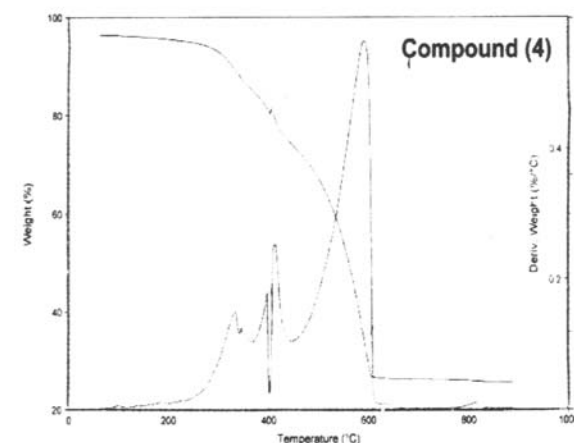
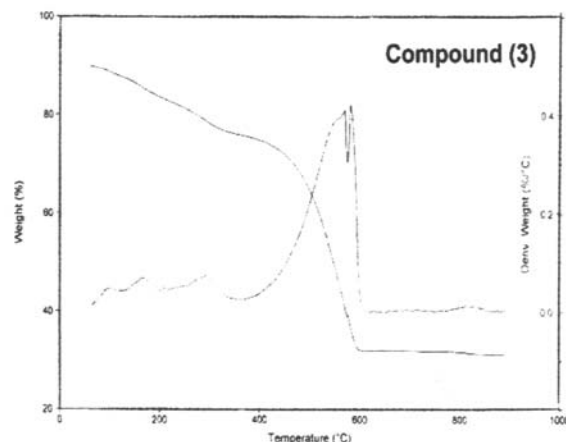


Fig. 6. TGA-DTA of compounds CuCl₂(OH)₂Ti₂(OiPr)₆ (3) and CuCl₂(OH)₂Si₂(OEt)₆ (4), done under nitrogen with a heating ramp of 10 °C min⁻¹. Thermal decomposition starts at 590 °C y 560 °C respectively.

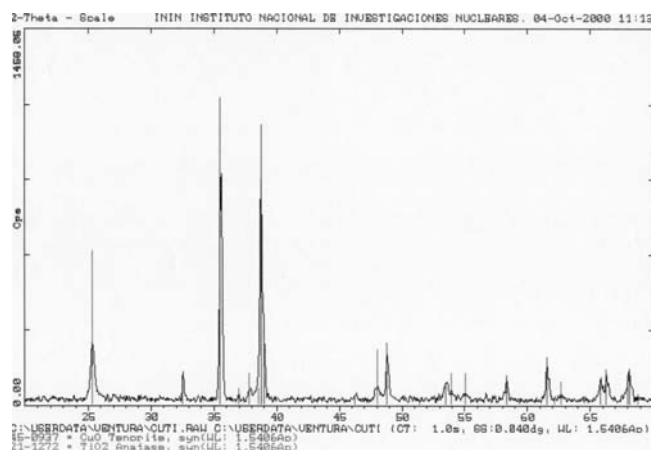


Fig. 7. X Ray diffractogram from the pyrolysis product of CuCl₂(OH)₂Ti₂(OiPr)₆ (3). It shows the presence of CuO as tenorite and the phase anatase for TiO₂.

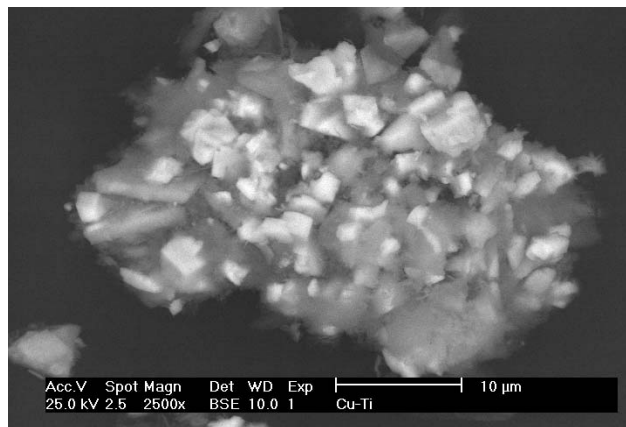


Fig. 8. Micrograph from the pyrolysis product of $\text{CuCl}_2(\text{OH})_2 \cdot \text{Ti}_2(\text{OiPr})_6$ (3). It shows CuO crystals from 3 and up to $10 \mu\text{m}$ embedded in the TiO_2 matrix.

General synthetic procedure:

Compounds were prepared by refluxing for 5 h 5 mmol of CrCl_3 or $\text{CuCl}_2(\text{H}_2\text{O})_2$ with 25 mmol of TEOS or TIPO in 40 mL of toluene.

$\text{CrCl}_3 \cdot \text{Ti}(\text{OiPr})_4$ (1): Dark red microcrystalline powder, unstable to humidity. I.R. ($\text{KBr}, \text{cm}^{-1}$): 1380, 1136, 1102, 614, 548. Mag. Suscep.: 1.26×10^{-5} c.g.s. Anal. C. (%): C: 32.6, H: 6.34, Cl: 24.1, Cr: 11.8, Ti: 10.7. Anal. Exp (%): C: 31.5, H: 5.84, Cl: 23.6, Cr: 10.9, Ti: 9.84.

$\text{CrCl}_3 \cdot \text{Si}(\text{OEt})_4$ (2): Fuchsia microcrystalline powder, unstable to humidity. I.R. ($\text{KBr}, \text{cm}^{-1}$): 1447, 1405, 1085, 1024, 872, 536. Mag. Suscep.: 1.94×10^{-5} c.g.s. Anal. C. (%): C: 26.2, H: 5.46, Cl: 29.1, Cr: 14.2, Si: 7.64. Anal. Exp (%): C: 25.5, H: 5.25, Cl: 28.6, Cr: 13.2, Si: 7.50.

$\text{CuCl}_2(\text{OH})_2 \cdot \text{Ti}_2(\text{OiPr})_6$ (3): Dark green microcrystalline powder, unstable to humidity. I.R. ($\text{KBr}, \text{cm}^{-1}$): 3270, 1365, 1120, 1017, 932, 860, 738, 667. Mag. Suscep.: 5.01×10^{-6} c.g.s. Anal. C. (%): C: 35.0, H: 7.10, Cl: 11.5, Cu: 10.3, Ti: 15.5. Anal. Exp (%): C: 32.3, H: 6.83, Cl: 10.5, Cu: 9.65, Ti: 13.9.

$\text{CuCl}_2(\text{OH})_2 \cdot \text{Si}_2(\text{OEt})_6$ (4): Dark yellow microcrystalline powder, unstable to humidity. I.R. ($\text{KBr}, \text{cm}^{-1}$): 3288, 1620, 1586, 1459, 1076, 722. Mag. Suscep.: 6.55×10^{-6} c.g.s. Anal. C. (%): C: 29.1, H: 6.47, Cl: 14.4, Cu: 12.8, Si: 11.3. Anal. Exp (%): C: 27.5, H: 5.92, Cl: 13.6, Cu: 11.9, Si: 10.8.

Concluding Remarks

It has been shown that regular ligands such as TEOS and TIPO are able to bond to CrCl_3 by oxygen free electron pairs. This influences the decomposition temperatures of the obtained compounds, which are relatively low and close to the

boiling points of the ligands. Pyrolysis under oxygen at $500 \text{ }^\circ\text{C}$ for these compounds yields composites of crystalline eskolaite and amorphous SiO_2 or TiO_2 .

TEOS and TIPO are also able to bond to $\text{CuCl}_2(\text{H}_2\text{O})_2$ through partial hydrolysis of these alkoxides induced by the water molecules bound to the copper(II) ion.

Compounds produced with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ have decomposition temperatures three times higher than those observed for the case of CrCl_3 . This is indicative of a covalent bond metal-ligand established during the hydrolysis. The products obtained when these two compounds were burnt under oxygen at $500 \text{ }^\circ\text{C}$ form crystalline composites of tenorite and anatase (with TIPO) and a composite of crystalline tenorite with amorphous SiO_2 (with TEOS).

Thus, it is possible with simple reactions, to coordinate the TEOS and TIPO molecules to the chromium(III) and copper (II) ions, obtaining potential precursors for composites based on metallic oxides.

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