

SOME POLYNUCLEAR COORDINATION COMPOUNDS PRECURSORS OF CHROMITES

Synthesis, physicochemical characterization and thermal stability

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Abstract

The polynuclear coordination compounds $\text{LnCr}(\text{tartrate})_3 \cdot n\text{H}_2\text{O}$ where $\text{Ln(III)}=\text{La-Er}$, obtained through a precipitation method, were characterized on the basis of elemental analysis, their electronic and vibrational spectra and magnetic susceptibility measurements. The possibility of obtaining chromites through the transformations of the polynuclear coordination compounds in the solid state was considered. The thermal decompositions of these compounds, studied by TG and DTA methods, were found to follow an almost uniform pattern. The decompositions occurred in six–eight steps. The first two steps involved dehydration, and the third the transformation of tartrate anions to oxalate, followed by conversion to carbonate and oxocarbonate intermediates. The final product in each case was LnCrO_3 . A non-isothermal kinetic analysis of the first decomposition steps was performed, the most probable decomposition mechanism being selected and the kinetic parameters evaluated. The final products of the transformations were characterized.

Keywords: chromites, polynuclear coordination compounds, precursors

Introduction

The literature frequently reports the use of mixed oxides containing lanthanide and transition metals as catalysts in redox reactions [1], in hydrogenation reactions [2] and as automobile exhaust catalysts [3] with high catalytic activity.

In order to avoid the difficulties encountered in the ceramic method [4], in recent years new nonconventional methods have been developed, such as the ther-

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mal decomposition of metal-organic and polynuclear [5] coordination [6–9] precursors.

Experimental

Synthesis

Polynuclear coordination compounds were separated from the reaction media (solutions containing Ln(III)-Cr(III)-tartaric acid) by extraction with ethanol. For complete precipitation, 24 h was necessary, together with repeated adjustment of the pH to 5.5–6 by the addition of 20% NH₄OH solution. The fine-crystalline products that separated out were filtered off, washed with ethanol and dried. The synthesis method used was a version of the method of Melson and Pickering [11]. The products obtained, with colours ranging from light-blue through grey and grey-green to green, are soluble in water, but insoluble in most organic solvents.

Elemental analysis

The coordination compounds were subjected to quantitative analysis: the metal contents were determined by atomic absorption techniques, and the carbon and hydrogen contents by using a combustion method coupled with chromatographic techniques.

Spectral measurements

The UV-VIS reflectance spectra were recorded at room temperature on a Speccord M 40 spectrophotometer, in the range 11.000–54.000 cm⁻¹.

The IR spectra of the polynuclear compounds were obtained by applying the KBr pellet technique in the range 400–4.000 cm⁻¹, using a Speccord M-80 infrared spectrophotometer.

X-ray powder diffraction

The state of crystallinity of the compounds used and the decomposition products were investigated by means of a Dron 3 X-ray diffractometer, with CoK_α radiation.

Thermal measurements

The thermal decomposition curves were investigated with a Q-1500 D Paulik-Paulik-Erdey derivatograph in a static air atmosphere at heating rates in the range 2.5–5 K min⁻¹, with a sample mass of 50 mg, in ceramic crucibles, with α-Al₂O₃ as reference compound. The values of non-isothermal kinetic parame-