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THERMAL STUDY OF TiO_2–CeO_2 YELLOW CERAMIC PIGMENT OBTAINED BY THE PECHINI METHOD

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TiO_2–CeO_2 oxides for application as ceramic pigments were synthesized by the Pechini method. In the present work the polymeric network of the pigment precursor was studied using thermal analysis. Results obtained using TG and DTA showed the occurrence of three main mass loss stages and profiles associated to the decomposition of the organic matter and crystallization. The kinetics of the degradation was evaluated by means of TG applying different heating rates. The activation energies (E_a) and reaction order (n) for each stage were determined using Horowitz–Metzger, Coats–Redfern, Kissinger and Broido methods. Values of E_a varying between 257–267 kJ mol^{-1} and n=0–1 were found. According to the kinetic analysis the decomposition reactions were diffusion controlled.

Keywords: *kinetic study, mixed oxide, Pechini method*

Introduction

Ceramic pigments coloring inorganic substances that do not react chemically with the host matrix and stay stable at high firing temperatures. Besides, they have to have suitable particle size distribution, good resistance to acids, alkalines and abrasives, as well as good thermal stability is also an important requirement [1].

Several methods have been developed to obtain pigments with these characteristics [2, 3]. Among them the Pechini method is important due to its simplicity and easy performance [4].

In the Pechini method some metal-ion chelate forming carboxylic acids are used. Those metal chelates are polyestherified when heated in polyhydroxyl alcohols resulting a resin in which the ions are immobilized and the desired oxides are obtained by heat treatment. The method provides homogeneous powders with small particle size, high purity, low cost and relatively low processing temperature [4].

The physical transformations and chemical reactions which undergo in the sample upon heating are characteristic to each substance which is the target of examination. The temperature measurement of the transformation reactions allows characterizing the compounds present in the starting material. These changes also indicate the temperature where the sample becomes stable under standard conditions [5]. In this way, understanding of the physical transformations and chemical reactions that take place during the burning of the polymeric network leads to characterization of the resultant compounds and provides information for future synthesis of advanced ceramics [6].

Several authors [7–9] studied the thermal decomposition behavior of these resins in order to characterize the resulting products and improve the synthesis conditions, but the published papers concerning this kind of investigation using these techniques are very scarce.

In this work the thermal degradation process of the polymeric resin precursors of TiO_2–CeO_2 was investigated using thermal analysis (TG and DTA). The activation energy (E_a) as well as the reaction order (n) of the processes was calculated using various kinetic models.

Experimental

Synthesis of the TiO_2–CeO_2 pigment

The TiO_2–CeO_2 (CeO_2=10 mol%) pigment was synthesized using the Pechini method according to the steps described in Fig. 1. The molar ratio between the citric acid and the metal cation was 3:1 while the ratio between citric acid and ethylene–glycol was 1:2.

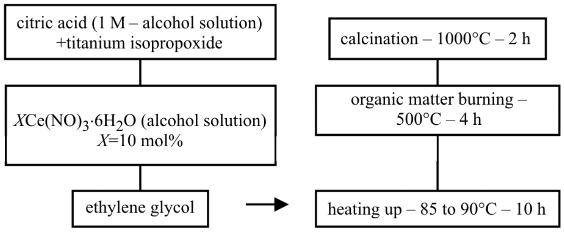

Fig. 1 Scheme of synthesis of TiO_2–CeO_2 pigment

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Instrumentation

The crystal structure of the resultant powders was determined by X-ray diffraction using Bruker-AXS D5005 diffractometer, CoK_α radiation (35 kV/40 mA) in the 5–80° 2θ range.

The thermal analyses (TG/DTA) were carried out using Shimadzu TA-50WSI thermobalance and DTA-50 unit at 10°C min^{-1} heating rate up to 1200°C in air.

TG data treatment

The TG curves were recorded at three different heating rates: 5, 10 and 20°C min^{-1}. The obtained results were used to calculate the activation energy (E_a) at each thermal decomposition stage. Four kinetic models were used to evaluate the thermal degradation kinetics:

Horowitz–Metzger relation [10]:

$$\ln\left[\ln\frac{W_0-W_f}{W-W_f}\right]=\frac{E_a\theta}{RT_S^2} \qquad (1)$$

where W_0 is the initial mass of the sample, W_f is the final mass of the sample, W is the mass of the sample at a given temperature T, E_a is the activation energy, $\theta=T-T_s$ (T_s=maximum temperature of the DTG curve).

Coats–Redfern relation [10]:

$$\ln\left[\ln\frac{(1-\alpha)}{T^2}\right]=-\frac{E_a}{RT} \qquad (2)$$

where α is the decomposed fraction at temperature T, T^2 is the maximum temperature of the DTG curve and R is the gas constant.

Kissinger relation [11]:

$$\ln\left(\frac{q}{T_{max}^2}\right)=-\frac{E_a}{RT_{max}} \qquad (3)$$

where q is the heating rate, T_{max} is the maximum temperature of the DTG peak.

Broido relation [11]:

$$\ln\left[\ln\left(\frac{1}{Y}\right)\right]=-\frac{E_a}{RT} \qquad (4)$$

where Y is the fraction of the undecomposed initial molecules.

Kinetic models for solid-state reactions were used to evaluate the reaction order and the decomposition mechanisms according to [12].

Results and discussion

Figure 2 shows the TG and DTA curves of the polymeric resin precursor of the TiO_2–CeO_2 pigment. The TG curve indicates four mass loss steps, where the first between 30–200°C leads to 20.6% of mass loss due to the elimination of physically adsorbed water and the alcohol (used for solvent). In the second and in the third regions (50% mass loss) from 200 to 380°C was recorded because of the organic matter combustion. Finally, the fourth one between 380 and 520°C with 11.9% of mass loss was associated to the elimination of chemically bound water in the solids and the decomposition of the residual organic matter [13].

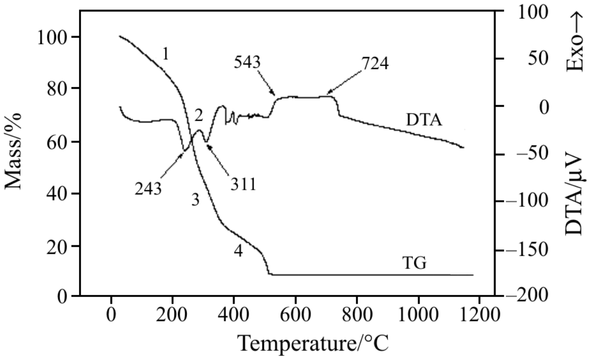

Fig. 2 TG and DTA curves of the precursor resin of the TiO_2–CeO_2

The findings based on the TG curves were supported by the DTA curves as well (Fig. 2b), where endothermic peaks were found in the 200–500°C region which are related to decomposition of the organic matter (243 and 311°C) [5, 13, 14].

The exothermic peaks at 543 and 724°C were associated to the formation of crystalline TiO_2 from amorphous state and to the phase transformation to rutile, respectively, as confirmed by X-ray diffraction analysis (Fig. 3). The analysis also pointed to the presence of peaks representative to the cerium dioxide enabling to characterize the compound as a mixed-oxide of cerium and titanium.

Figure 4 shows the DTG curve corresponding to the 2 and 3 regions 2 where two distinct mass loss processes can be clearly identified with peak maxima at 257 and 319°C.

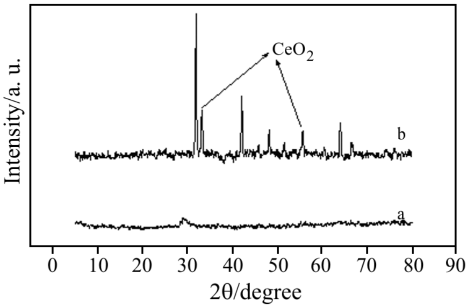

Fig. 3 X-ray diffraction patterns of a – TiO_2–$0.1CeO_2$ burned at 500°C and b – TiO_2–CeO_2 calcined at 1000°C

Table 1 Activation energy (E_a) and correlation coefficients calculated by HM (Horowitz–Metzger), CR (Coats–Redfern), Br (Broido) and Ks (Kissinger) methods

Stage	E_a/kJ mol^{-1}				R			
	HM	CR	Br	Ks	HM	CR	Br	Ks
2	214.4	183.8	209.5	87.3	0.99547	0.99404	0.99346	0.99349
3	276.2	279.5	269.8	257.8	0.99731	0.99791	0.99509	0.99947

Regions 2 and 3 of the thermal decomposition were submitted to a non-isothermal kinetic study in order to investigate the reaction order, activation energy and decomposition mechanism. Table 1 presents the obtained activation energy values.

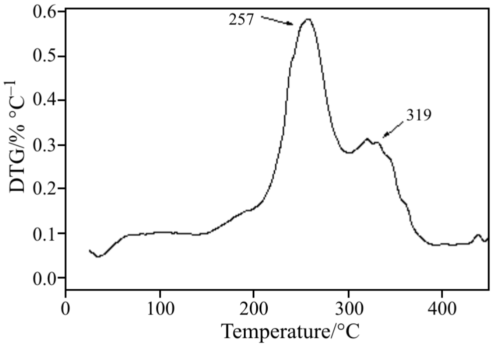

Fig. 4 DTG curve of the precursor resin of the TiO_2–CeO_2 pigment

In the second mass loss stage a variation between 87 and 214 kJ mol^{-1} was observed. Results obtained by the Kissinger method were in disagreement with the results of other methods. This can be explained by the fact that the Kissinger method does not consider reaction order in the calculation of the activation energy, providing not so confident data when the reaction order is different of 1.

In the third stage the E_a values varied between 257 and 276 kJ mol^{-1} and a good agreement between the different methods was found. This stage presents higher activation energy. The DTG profile analysis suggests that during the thermal decomposition the cleavage of the polymeric resin into smaller molecules occurs at first and just in this stage (at 280°C) the decomposition of the organometallic part takes place (having higher thermal stability and consequently higher activation energy).

The thermal decomposition mechanism was investigated according to [12]. The obtained results showed that the best fitting equations were corresponding to the zero order reaction for the second stage and first order reaction for the third stage. It was verified that the decomposition mechanism is dominated by the occurrence of diffusion reactions, since D1 and D2 models presented the best correlation coefficients.

In a future work, infrared spectroscopy will be used to characterize the compounds formed in each step of the decomposition process and this data will be correlated with the results of present paper.

Conclusions

Thermal decomposition process of the polymeric network precursor of the TiO_2–CeO_2 pigment was characterized by thermal studies.

The kinetics analysis showed that activation energies were between 87–214 kJ mol^{-1} for the second stage of the decomposition and in between 257–276 kJ mol^{-1} for the third stage applying Horowitz–Metzger, Coats–Redfern, Broido and Kissinger methods.

First and zero order reaction mechanism and diffusion controlled reactions took place in the thermal decomposition process of the polymeric resin.

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