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SYNTHESIS AND CHARACTERIZATION OF A HYDRATED TITANIUM(IV) OXIDE

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ABSTRACT

By adding an aqueous solution of sodium hydroxide to a sulphuric solution of titanium(IV), the compound $TiO_2 \cdot nH_2O$ was obtained, the value of n being approximately 1. The precipitation was accompanied by an exothermic reaction which indicated that the precipitate always formed at temperatures of $\approx 90\,^\circ C$. The X-ray diffraction pattern of this compound shows a poorly crystallized anatase. There was no observed phenomenon in the DTA curve during the anatase–rutile transition, probably because the transition was immeasurably slow. When the heating rate was $300\,^\circ C\ h^{-1}$, both phases coexist in the approximate temperature range 700–900 °C.

INTRODUCTION

The numerous technological applications of the titanium oxides as dielectric ceramic materials, inorganic ion exchangers, sorbents or pigments, have given rise to their numerous preparation methods. The method most frequently employed is precipitation from chloric or sulphuric solutions of titanium(IV) to which has been added an aqueous solution of ammonia or sodium hydroxide. Other methods are the thermal hydrolysis of an aqueous solution of controlled acidity or the hydrolysis of titanium alkoxide in alcohol solution. In all the methods a white gelatinous precipitate is obtained, but each author gives it a different formula (see Table 1).

EXPERIMENTAL

Materials

Titanium (fine powder form), H_2SO_4 (95–97%) and NaOH, all from Merck, AnalaR quality, were used.

TABLE 1

Alkaline precipitation of titanium(IV)

Formula of the precipitate	Authors
$TiO_2 \cdot H_2O$	Pascal (1963) [1]
$TiO_2 \cdot 2H_2O$	Pascal (1963) [1] Tishchenko and Koko (1970) [2]
$TiO_2 \cdot nH_2O$	Popkovich and Sviridov (1975) [3] Akhmanova et al. (1977) [4] Zhao (1982) [5] Sharygin et al. (1982) [6] Dvernyakova et al. (1981) [7]
$TiO(OH)_2$	Dvernyakova et al. (1981) [7] Packter and Derry (1986) [8]
$Ti(OH)_4$	Díaz-Güemes et al. (1988) [9]
$TiO_{2-x}(OH)_{2x} \cdot yH_2O$	Vivien et al. (1970) [10]
$nTiO_2 \cdot mH_2O \cdot (1-n)(TiO(OH)_2)$	Arginbaev et al. (1974) [11]
$TiO_2 \cdot nH_2O + TiO(OH)_2 \cdot nH_2O$	Saraswat et al. (1986) [12]

Preparation of the sample

The sulphuric solution of Ti^{4+} was prepared by boiling a weighed amount of finely powdered titanium with 2N H_2SO_4 and a few drops of concentrated nitric acid until dissolved.

To the strongly acidic sulphuric solution of titanium was added, drop by drop, concentrated aqueous sodium hydroxide, producing a strongly exothermic reaction such that the temperature of the solution was raised to approximately 90 ° C. The solution was stirred rapidly during the addition of sodium hydroxide and the pH was controlled with a pH meter.

The addition of sodium hydroxide produced a gradual increase in pH up to pH 4; from pH 4 to 7 a sudden rise was observed, and at pH 7 the precipitation was complete.

The white gelatinous precipitate obtained was collected by filtration on a No. 4 porosity filter. The filtrate was analysed for titanium using 2% chromotropic acid; the analysis was negative, showing that the precipitation was quantitative.

The precipitate was washed with cold distilled water until no sulphate was present in the washings. Using atomic absorption spectrophotometry, the washed precipitate was shown to be free of sodium ions.

The precipitate was dried at room temperature, ground (grain size 95–47 μm) and kept in closed vessels.

Apparatus

Thermogravimetric (TG) analysis

A Mettler TA 3000 system with TG50 attachment was used, at a heating rate of 600 °C h^{-1}.

Differential thermal analysis (DTA)

A laboratory-constructed system incorporating a vertical furnace and a temperature regulation system, both from Adamel, and a differential chromel–alumel thermocouple were used. The heating rate was 300 °C h^{-1}.

X-ray powder diffraction

A Philips PW 1130 diffractometer was used, with a Ni filter and Cu $K\alpha_1$ radiation.

IR spectroscopy

A Perkin–Elmer model 683 spectrophotometer was used. The sample was prepared as a mull using Fluorolube as mulling agent for examination in the region 4000–1500 cm^{-1}, and KBr pellets for the region 1500–200 cm^{-1}.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of the precipitate obtained under the experimental conditions mentioned above corresponds to poorly crystallized anatase (Fig. 1a).

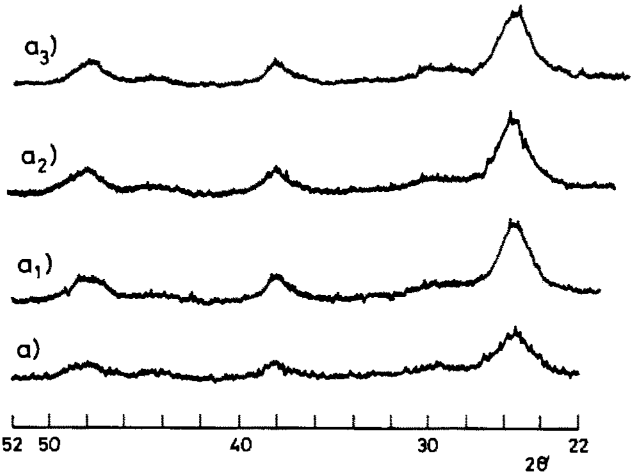

Fig. 1. X-ray diffraction patterns: a, precipitate dried at room temperature; a_1, a_2 and a_3, precipitate calcinated for 2 h at 70, 90 and 110 °C, respectively.

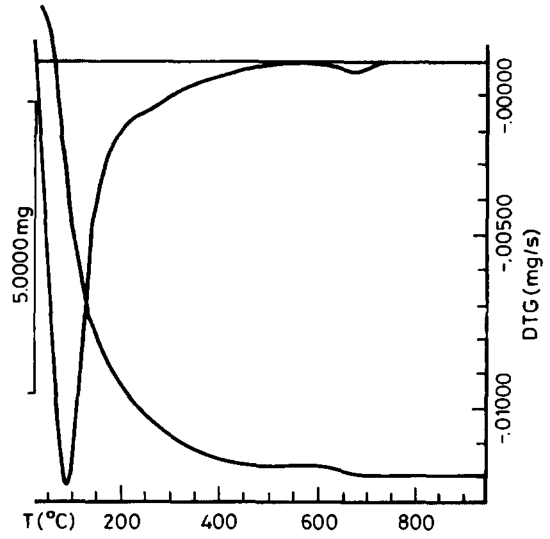

Fig. 2. TG and DTG curves of the precipitate. Sample weight 37.397 mg.

The majority of the authors who have studied this precipitate have stated that the air-dried precipitate [6,10,13,14], dried at 80 °C [12] or at 100 °C [15] had an amorphous structure. It was necessary to heat the sample to higher temperatures to obtain crystals of anatase: at 160 °C coarse crystals were obtained [16]; at 250 °C ill-defined anatase crystals were obtained [14,15]. On the other hand, the samples studied in ref. 13 remained amorphous after heating up to 400 °C. We believe that the presence of anatase in our precipitate was due to the fact that the precipitate was obtained at ≃ 90 °C, showing once more the influence of the precipitation procedure on the characteristics of the samples obtained.

Thermal analysis

The thermal study by TG and DTA has given consistent qualitative results.

Below 600 °C, the TG and DTG curves, see Fig. 2, show an initial large loss. The total weight loss was 21% with respect to initial weight.

A small loss of about 1% of the initial weight, occurring between 600 and 800 °C, was due to the small quantity of sulphate impurities retained in the precipitate; (this was also observed by Yoganarasimhan and Rao [15]).

The dehydration of the sample took place in a single step at low temperature, which suggests the presence of water hydration; the compound studied here was a hydrated oxide, $TiO_2 \cdot nH_2O$, the value of n being approximately 1. The sample was not altered with time: after 46 months the formula was $TiO_2 \cdot 1.02H_2O$ and its X-ray pattern was unchanged.

TABLE 2

TiO_2/H_2O ratio at different temperatures

Samples	Temperature of calcination (° C)	TiO_2/H_2O ratio
a_1	70	1/0.61
a_2	90	1/0.52
a_3	110	1/0.43

Pascal [1], in his review of the first studies concerning the precipitation of titanium(IV), said that the precipitated compound, titanium dioxide, had the formula $TiO_2 \cdot 2H_2O$ when the precipitation was carried out at room temperature, while if the precipitation took place at boiling point the formula would be $TiO_2 \cdot H_2O$.

Our results agree with the last case: the precipitation was accompanied by exothermic reaction which meant that the precipitate was always formed at $\approx 90\,°C$.

The degree of hydration of titanium(IV) oxides is very variable, and depends on the preparation, especially the drying temperature of the precipitate. Whatever the ratio, TiO_2/H_2O is a function of the temperature of heating of the precipitate and it is not altered with time. For that reason, the composition attributed to the precipitate is different, as is clear from Table 1.

The precipitate $TiO_2 \cdot 1.02H_2O$ obtained using the experimental conditions mentioned above, was heated for 2 hours at three different temperatures (70, 90 and 110 ° C). In all cases the sample reached a constant weight and the TiO_2/H_2O ratio slowly decreased in proportion to the increased temperature of calcination, see Table 2.

The X-ray diffraction patterns a_1, a_2 and a_3 of Fig. 1 are identical to the pattern of the sample without calcination (Fig. 1a).

The DTA curve, Fig. 3, shows a single endothermic peak, $T_t = 160\,°C$, due to the dehydration of the sample.

Figure 4 shows the X-ray patterns corresponding to the samples taken at 350, 500, 600 and 700 ° C in the DTA curve (Fig. 3). It is evident from Fig. 4

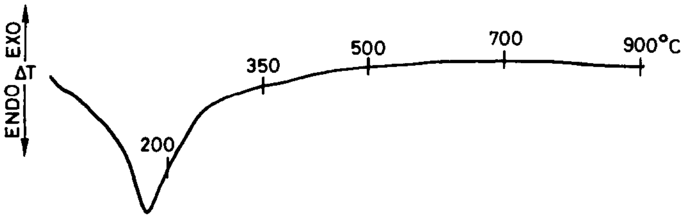

Fig. 3. DTA curve of the precipitate.

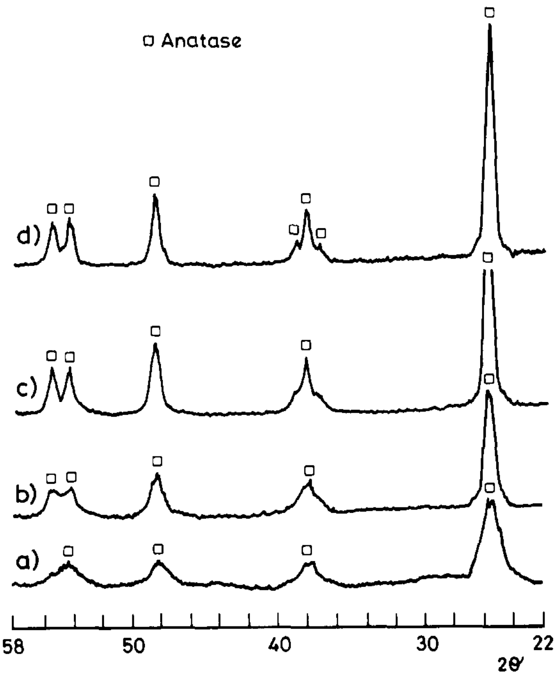

Fig. 4. X-ray diffraction patterns of the precipitate: a, at 350 °C; b, at 500 °C; c, at 600 °C; d, at 700 °C.

that anatase is better crystallized when the temperature of calcination is higher.

Figure 5 shows the X-ray patterns corresponding to the samples taken at 750, 850 and 900 °C in the DTA curve (Fig. 3). At 750 °C, rutile appears and at 850 °C rutile predominates and anatase appears as an impurity. At 900 °C, the X-ray pattern indicates only rutile.

The anatase–rutile phase transition, using the experimental conditions reported here, took place in a 200 °C temperature interval (from 700 to 900 °C approximately) which was equivalent to forty minutes from the beginning of the transition until the end.

Numerous authors have talked of the slowness of this process: Czanderna et al. [16] studied the kinetics of the transformation of pure anatase and found that below 610 °C the transition was immeasurably slow; Jere and Patel [14] found that the rate of conversion was slow at 600 °C.

Yoganarasimhan et al. [15] studied an anatase prepared by the hydrolysis of titanium sulphate, and found that the anatase–rutile transformation occurred at a much higher temperature than that of pure anatase, possibly due to the presence of a sulphate ion impurity in the sample: the transformation became immeasurably slow below $\simeq 695 \pm 10$ °C. Our results confirmed these values.

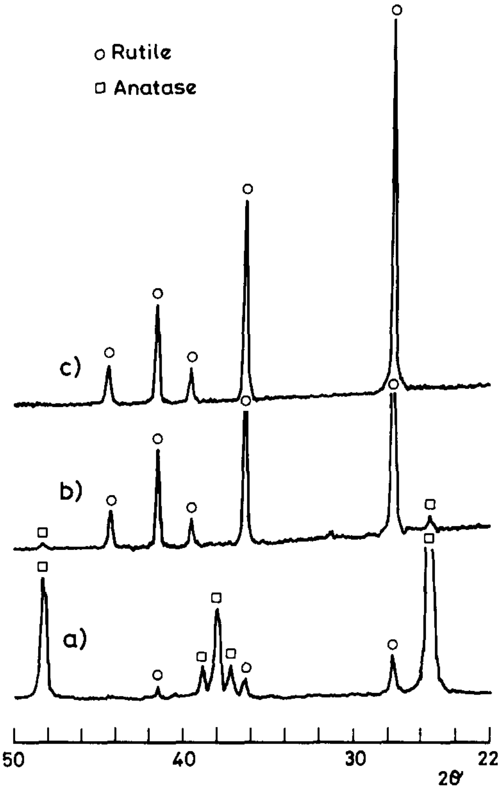

Fig. 5. X-ray diffraction patterns of the precipitate: a, at 750 °C; b, at 850 °C; c, at 900 °C.

In our opinion, differential thermal analysis (DTA) does not detect the anatase–rutile transition because the energetic change is very small and very slow. (The formation values of both crystalline species [17] are anatase, $\Delta H_{f298.15} = -218.1$ kcal mol^{-1}; and rutile, $\Delta H_{f298.15} = -225.5$ kcal mol^{-1}.)

A few authors have used differential thermal analysis (DTA) to study the oxides of titanium(IV). Only three have found a shallow exothermic peak at 600 °C. Heitner-Wirguin and Albu-Yaron [13] attributed it to the decomposition of the remaining traces of oxalate, $K_2TiO(C_2O_4)_2$, the solution of origin, while Jere and Patel [14] and Vivien et al. [10] believed that this peak corresponded to the slow irreversible conversion of the tetragonal lattice of anatase into the tetragonal lattice of rutile.

Infrared spectroscopy

The greatest discrepancy in the interpretations of the different authors surrounds the presence or absence of a metal–hydroxyl linkage in this compound.

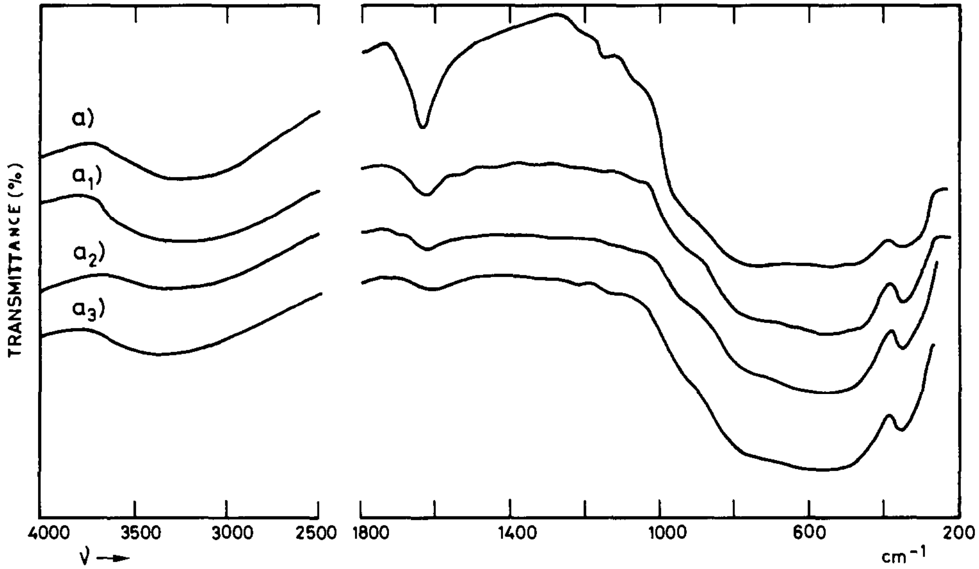

Fig. 6. IR spectra: a, precipitate dried at room temperature; a_1, a_2 and a_3, precipitate calcinated for 2 h at 70, 90 and 110 °C, respectively.

For the dehydration of the precipitate, some authors have given, a priori, equations of the following type

$TiO(OH)_2 \rightarrow TiO_2 + H_2O$ [8]

$Ti(OH)_4 \rightarrow TiO_2 + H_2O$ [9]

Using nuclear magnetic resonance, Tishchenko and Koko [2] established that in the precipitate $TiO_2 \cdot 2H_2O$, 13–14% of the hydrogen was in hydroxyl form. Then, following differential thermal analysis (DTA), they concluded that the first dehydration of the compound leads to the formation of $TiO(OH)_2$. The majority of authors, however, used IR spectroscopy [10,12–14,18].

In the spectra given by these authors, the wide asymmetric band appearing at about 3100–3400 cm^{-1}, was attributed to the OH stretching vibration of water and hydroxyl group. Moreover, the band at 1640 cm^{-1}, due to the H–O–H bending motion was always present.

The spectrum of the precipitate of $TiO_2 \cdot H_2O$ obtained in the present study is shown in Fig. 6, spectrum a.

We believe that the wide, very strong band at 3400 cm^{-1}, in spite of its asymmetry, corresponds exclusively to the stretching vibrations of water, due to the absence of a strong sharp absorption band in the region of 3650–3700 cm^{-1} characteristic of the hydroxyl group [19]. Also, the band corresponding to H–O–H bending at 1640 cm^{-1} is present.

In the 1000–250 cm^{-1} region, there is a strong absorption band at 570 cm^{-1} and a sharp band at 350 cm^{-1}. Both bands could be attributed to the bending vibrations of titanium–oxygen, $\nu_{Ti-O-Ti}$ [15,20].

The spectra a_1, a_2 and a_3 in Fig. 6 correspond to the samples described in Table 2. These spectra are practically identical to spectrum a in Fig. 6. In the spectra a_1, a_2 and a_3, the intensity of the bands of the stretching and bending vibrations of water decrease in proportion to the decreasing amount of water in the respective samples.

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