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THERMAL CHARACTERIZATION OF LAMELLAR TITANATES

*V. A. Cardoso[1], Liliane M. Nunes[1], J. C. O. Santos[2], Iêda M. G. Santos[1], Marta M. Conceição[3], J. R. Santos Jr.[4] and A. G. Souza[1]**

[1]Departamento de Química, CCEN, Universidade Federal da Paraíba, Campus I, 58059-900, João Pessoa, PB, Brazil
[2]Departamento de Química, CCT, Universidade Estadual da Paraíba, Campus I, Bodocongó, 58109-790, Campina Grande, PB, Brazil
[3]Departamento de Química, Universidade Federal do Rio Grande do Norte, Campus Universitário, 59072-970, Natal, RN, Brazil
[4]Departamento de Química, Universidade Federal do Piauí, Teresina, PI, Brazil

The alkaline lamellar titanates ($K_2Ti_4O_9$ and $Na_2Ti_3O_7$) obtained from solid state reactions react with acid solutions producing a partial ion exchange of the ions K^+ and Na^+ present in the interlamellar region by protons H^+, producing the titanate acid forms. These materials were characterized by X-ray diffraction, infrared spectroscopy and thermal analyses (TG/DTA).

Keywords: DTA, thermogravimetry, titanates

Introduction

Due to the great interest, several researchers have been investigating several aspects of lamellar titanates, such as intercalation properties, ion exchanges, preparation of adsorbing materials, as well as the possible application of titanium and titanates in the fibrous and lamellar forms [1, 2].

Facing to the countless existing forms of titanates, the following applications can be mentioned as examples: vitreous enamels, oxygen sensors, electrodes, ceramic additives, catalysts and catalytic supports, ion exchangers, adsorbing materials, pigments [3–5].

This work has as objective to synthesize and to characterize, by means of thermoanalytical techniques (TG/DTA), the sodium and potassium titanates and their respective acid forms. Thermogravimetry was used for the evaluation of the mass loss of the compounds with the increase of temperature, besides being an alternative method for the determination of the amounts of water and intercalated amine. DTA allowed to verify the enthalpy transitions related to the mass loss of the material and to the physical transformations that occur upon heating.

Experimental

Synthesis of titanates

The titanates $K_2Ti_4O_9$ and $Na_2Ti_3O_7$ were obtained by solid state reactions, using stoichiometric amounts of titanium oxide and the respective sodium and potassium carbonates. The stoichiometric mixture was heated in an alumina crucible at 800ºC for 20 h. It was then ground and heated again at the same temperature for more than 20 h [6, 7]. The acid forms $H_2Ti_4O_9$ and $H_2Ti_3O_7$ were obtained by the K^+, Na^+/H^+ ion exchange [6, 7]. The mixture was heated at the temperature of 70ºC for 6 days in a flask, under magnetic stirring. During this treatment the acid solution was changed three times. The material was separated by centrifugation, washed with bidistilled water up to the 5–6 pH range and dried at 40ºC for 42 h.

Intercalation process

The intercalation process of octyldiamine ($H_2N(CH_2)_8NH_2$) within the lamellar titanates $H_2Ti_4O_9$ and $H_2Ti_3O_7$, was performed using a suspension containing 4.0 g of the respective titanates and 125 mL of a 0.3 M aqueous solution of octyldiamine. The system was kept under magnetic stirring in a flask for 8 days at room temperature. Soon after, the solid material was separated by centrifugation, washed with bidistilled water and dried at 30ºC for 42 h.

Characterization

The diffraction patterns of the compounds were obtained in an X-ray diffractometer (D5000, Siemens) in the range of $2\theta=3–50º$, with a 0.02° step and a step time of 2.0 s, using as radiation source the CuK_α.

The thermoanalytical techniques TG/DTA were carried out using a simultaneous thermobalance (SDT 2960, TA Instruments), at the temperature

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* Author for correspondence: agouveia@quimica.ufpb.br

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Table 1 XRD data of the lamellar titanates

Main phase	2θ/degree	*d*/pm	Diffraction plans	Secondary phases
$K_2Ti_4O_9$	10.1;14.33; 28.08	875; 619; 317	200; 201; 310	$K_2Ti_6O_{13}$
$H_2Ti_4O_9$	9.86; 24.21	892; 367	200; 110	$K_2Ti_6O_{13}$ TiO_2
$Na_2Ti_3O_7$	10.52; 15.84; 5.71	842; 560; 346	001; 101; 011	–
$H_2Ti_3O_7$	9.7; 11.15; 16.28	911; 798; 543	001; 100; 101	$Na_2Ti_6O_{13}$ TiO_2(anatase)

range from 25 to 1000ºC, with a heating rate of 20ºC min^{-1}, under a nitrogen flow of 100 mL min^{-1}.

The absorption spectra in the infrared area were obtained by a spectrophotometer (Bomem, MB-series), using KBr pellets, and operating at the 400 to 4000 cm^{-1} range.

Results and discussion

X-ray diffraction

Figure 1 and Table 1 illustrate the X-ray diffraction patterns of the crystalline structures of sodium trititanate, potassium tetratitanate and their respective acid forms.

Potassium tetratitanate ($K_2Ti_4O_9$) and its respective acid form ($H_2Ti_4O_9$) were confirmed by X-ray diffraction. Small amounts of a secondary phase, ($K_2Ti_6O_{13}$), were also observed. Probably, the secondary phase present in potassium tetratitanate is a consequence of the potassium volatilization during the synthesis, once this phase presents a lower potassium content. The titanates $K_2Ti_4O_9$ and $H_2Ti_4O_9$ display, in the studied range, the first reflections at 2θ=10.1 and 9.86º, with interplanar distances equal to 875 and 892 pm, respectively, corresponding to the (200) plane of the respective titanates. These interplanar distances are in agreement with data observed in the literature and they represent the interlamellar distance of the solid.

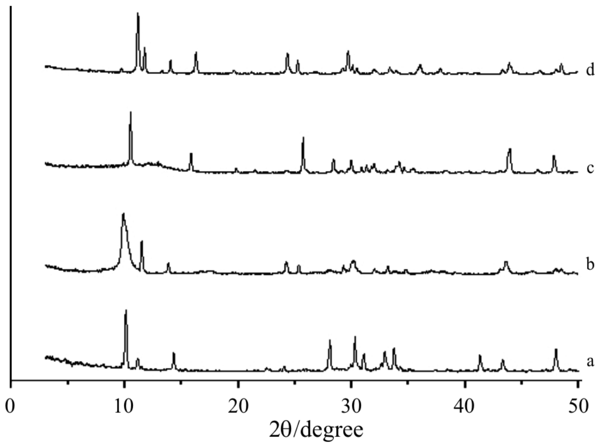

Fig. 1 X-ray diffraction patterns of the lamellar titanates: a – $K_2Ti_4O_9$, b – $H_2Ti_4O_9$, c – $Na_2Ti_3O_7$ and d – $H_2Ti_3O_7$

Figure 1c represents the diffraction pattern of a single phase material, related to the phase $Na_2Ti_3O_7$. Sodium trititanate ($Na_2Ti_3O_7$) and its acid form ($H_2Ti_3O_7$) display the first reflection at 2θ=10.52 and 9.70º, with interplanar distances of 842 and 911 pm, respectively.

The acid forms $H_2Ti_4O_9$ and $H_2Ti_3O_7$, the resulting products of the K^+, Na^+/H^+ ion exchange, present, besides the wanted phases, small amounts of a secondary phase. As these materials were obtained by means of ion exchange reactions, a possible distortion of the crystalline structure can cause the precipitation of some other phase. However, the presence of a small amount of $K_2Ti_6O_{13}$ in $H_2Ti_4O_9$ can be remained from its precursor.

The intercalation reaction consisted of the insertion of octyldiamine, $H_2N(CH_2)_8NH_2$, within the interlamellar space of the lamellar titanates $H_2Ti_4O_9$ and $H_2Ti_3O_7$. However, XRD data show that in the $H_2Ti_3O_7$ lattice did not occur the intercalation. The interlamellar distance of the modified lattice, as well as of the precursor lattice ($H_2Ti_4O_9$) is based on the interplanar distance related to the (200) plane reflection. The X-ray diffraction patterns presented in Fig. 2 show that the octyldiamine-intercalation process took place with an increase in the interlamellar distance of the material.

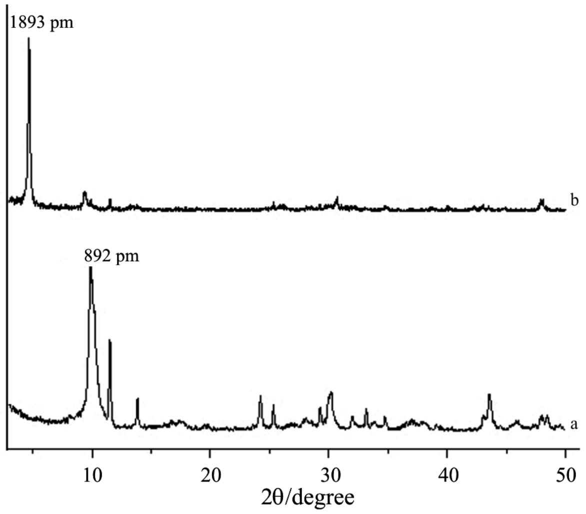

Fig. 2 Diffraction patterns of $H_2Ti_4O_9$ a – before and b – after the insertion of octyldiamine

The original ($H_2Ti_4O_9$) lattice that initially presented an interlamellar distance of 892 pm, after intercalation ($H_2Ti_4O_9$-octyldiamine) had this value raised to 1839 pm. In other words, an increase of 947 pm. The intercalation of octyldiamine does not affect the crystallinity of the original compound, what happens is a preferential orientation in the direction of the (200) plane, leading to an increase in the intensity of the peak related to this reflection.

Infrared spectroscopy

The results obtained with the elementary and infrared analyses confirm the existence of amine in the interlamellar area. The C, H, N elementary analysis yielded the mass percentages of 13.10, 3.56 and 3.70%, respectively, indicating an octyldiamine percentage of 19.42%.

The insertion of octyldiamine within the interlamellar space should lead to the appearance of new bands in the infrared absorption spectrum. The spectra for the compounds before and after intercalation are depicted in Fig. 3.

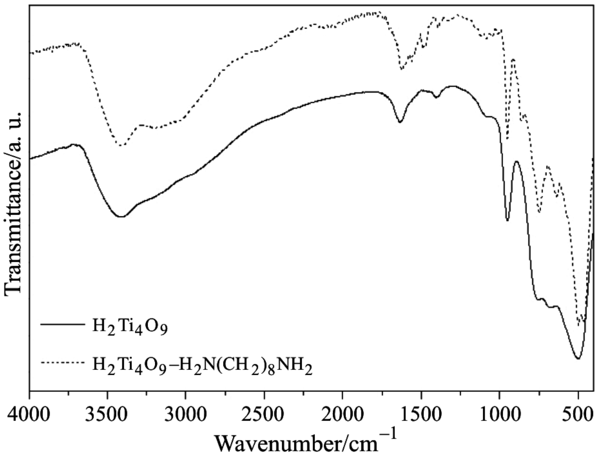

Fig. 3 Infrared $H_2Ti_4O_9$ spectra before and after the intercalation with octyldiamine

For the amine-intercalated compound, the spectrum shows the presence of peaks at 1559 and 1494 cm^{-1} that can be attributed to the angular deformation of the group NH^{3+}. The bands corresponding to the axial deformation of the group NH^{3+} that appears in the region between 3000–2800 cm^{-1} are not observed, due to the enlargement of this area provoked by the presence of water.

Thermal analysis (TG/DTA)

An important characteristic of these titanates and other lamellar materials is the fact that they are hydrated when exposed to the air. With the exception of $Na_2Ti_3O_7$, the other titanates presented thermal decomposition stages related to the exit of water. For the acid compounds, are observed decompositions at higher temperatures attributed to the exit of lattice water resulting from the condensation of OH groups.

Figure 4a refers to the thermal analysis of $Na_2Ti_3O_7$ and it does not exhibit any thermal decomposition stage. Conversely, $H_2Ti_3O_7$, Fig. 4c, displays a decomposition stage at around 180–580ºC equivalent to 4.56% of mass loss related to the exit of lattice water. The amount of water associated to this decomposition yields the approximate minimum formula, $H_{1.4}Na_{0.6}Ti_3O_7$, indicating that the K^+/H^+ exchange was not total. This material was heat treated at 600ºC and again analyzed by X-ray diffraction. The main product resulting from the dehydration of $H_{1.4}Na_{0.6}Ti_3O_7$ is TiO_2 (anatase). Also a small amount of $Na_2Ti_6O_{13}$ was observed, as a result of the dehydration process or remaining from the original material.

$K_2Ti_4O_9$, Fig. 4b, exhibits two small stages of mass loss, the first between 30–90ºC (0.43%) and one second between 90–390ºC (0.86%) related to the exit of respectively hydration water and interlamellar water. Interlamellar water refers to the absorbed water. The formula proposed for this compound becomes then, $K_2Ti_4O_9 \cdot 0.3H_2O$. The compound $H_2Ti_4O_9$ (Fig. 4d) presents the largest thermal decomposition, which takes place up to the temperature of approximately 600ºC.

Three thermal decomposition stages are observed. The first between 27–72ºC (0.97%) and the second between 72–144ºC (2.96%) are attributed to the exit of hydration water and interlamellar water, whereas the third stage between 144–600ºC (4.74%) is ascribed to the exit of lattice water (or constitution water). Based upon these data, the approximate minimum formula was calculated as $H_{1.9}K_{0.1}Ti_4O_9 \cdot 0.77H_2O$, for which it

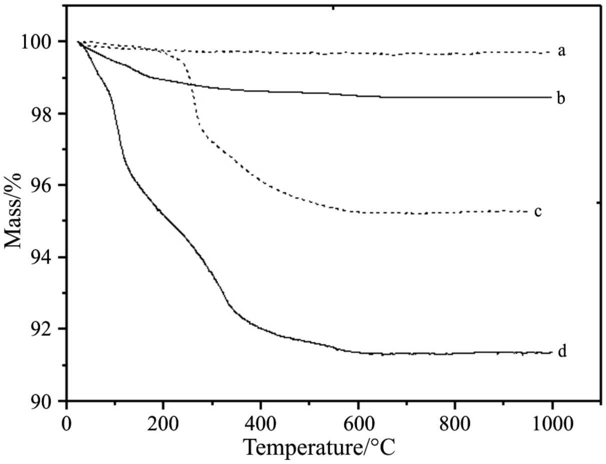

Fig. 4 TG curves for the a – $Na_2Ti_3O_7$, b – $K_2Ti_4O_9$, c – $H_2Ti_3O_7$ and d – $H_2Ti_4O_9$

is admitted that the K^+/H^+ exchange was almost total. The product resulting from the heat treating of this material at 600ºC is also TiO_2 (anatase) and a small amount of $K_2Ti_6O_{13}$.

According to the literature both $H_2Ti_3O_7$ and $H_2Ti_4O_9$, upon dehydration yield TiO_2 (brookite), which being submitted to a temperature higher than 350ºC, is rapidly transformed into TiO_2 (anatase) [8, 9]. Aiming at simplifying, the acid titanates will continue to be denominated as $H_2Ti_3O_7$ and $H_2Ti_4O_9$, although knowing that the Na^+, K^+/H^+ exchange was not total.

Analyzing the DTA curves (Fig. 5) together with the TG curves, additional information can be obtained regarding the mass loss and conformational changes.

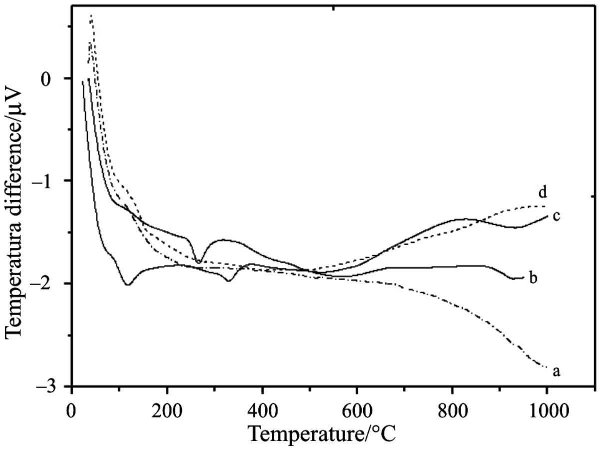

Fig. 5 DTA curves of a – $Na_2Ti_3O_7$, b – $H_2Ti_3O_7$, c – $H_2Ti_4O_9$ and d – $K_2Ti_4O_9$

The alkaline titanates ($Na_2Ti_3O_7$ and $K_2Ti_4O_9$) do not present defined peaks related to the thermal behavior. On the other hand, their acid forms ($H_2Ti_4O_9$ and $H_2Ti_3O_7$) show endothermic peaks between 250–350ºC that are attributed to the condensation process of interlamellar groups OH that arise from the formation of TiO_2 (brookite) [10]. An additional endothermic peak observed between 70–170ºC is ascribed to the dehydration process (hydration water) of $H_2Ti_4O_9$.

In Fig. 6 the thermogravimetric curves for $H_2Ti_4O_9$ are illustrated before and after intercalation. In the intercalated compound occurred the overlapping of the different thermal decomposition stages, not being possible to quantify the different losses. The overall decomposition took place at the temperature range between 30 and 950ºC, corresponding the thermal decomposition of the organic matter and water.

Moreover, in the precursor compound an overall mass loss of 8.67% is observed, whereas after intercalation the mass loss is of 27.7%, in other words, a difference of 19.03%. This mass loss percentage is approximately equal to the octyldiamine mass percentage observed in the elementary analysis (19.42%) being, therefore, one more indication of the presence of the amine in the interlamellar space.

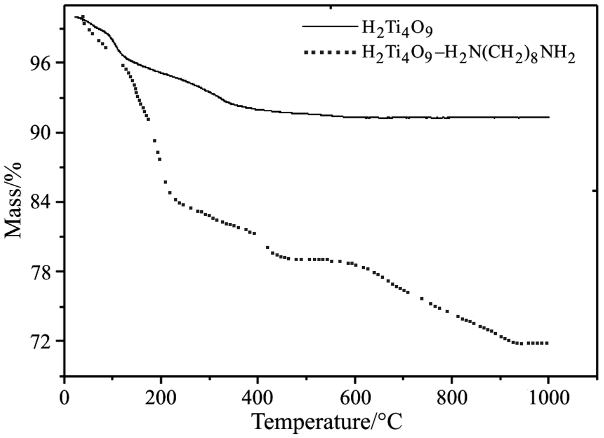

Fig. 6 TG curves of $H_2Ti_4O_9$ before and after intercalation with octyldiamine

Conclusions

For the materials obtained after ion exchange in the titanates $K_2Ti_4O_9$ and $H_2Ti_4O_9$, a small increase of the interlamellar distance was observed. Conversely, in $Na_2Ti_3O_7$ and $H_2Ti_3O_7$ a small contraction was verified.

The thermogravimetric curves for the acid forms of the titanates generally presented decomposition stages related to the exit of hydration water and interlamellar water. Their thermogravimetric curves present thermal behaviors that were similar to the ones of the original titanates, only varying the amounts of the water.

The intercalation reaction of octyldiamine, which consisted in the insertion of octyldiamine [$H_2N(CH_2)_8NH_2$] within the interlamellar space, only occurred in the $H_2Ti_4O_9$. The original titanate ($H_2Ti_4O_9$) that initially presented an interlamellar distance of 892 pm, after intercalation ($H_2Ti_4O_9$-octyldiamine) displays a distance of 1839 pm.

Acknowledgements

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References

1 A. Clearfield, Chem. Rev., 88 (1988) 125.
2 T. Sasaki, M. Watanabe, Y. Komatsu and Y. Fujiki, Inorg. Chem., 24 (1985) 2265.
3 S. B. C. Pergher, A. Corma and V. Fornes, Quim. Nova, 22 (1999) 420.

4 L. M. Nunes and A. G. Souza, J. Therm. Anal. Cal., 67 (2002) 365.

5 J. M. Criado, M. Gonzalez, A. Ortega and C. Real, J. Thermal Anal., 29 (1984) 243.

6 H. Izawa, S. Kikkawa and M. Koizumi, J. Phys. Chem., 86 (1982) 1324.

7 C. Airoldi, L. M. Nunes and R. F. Farias, Mater. Res. Bull., 35 (2000) 2081.

8 T. P. Feist and P. K. Davies, J. Solid State Chem., 101 (1992) 275.

9 T. P. Feist, S. J. Mocarski, P. K. Davies, A. J. Jacobson and J. T. Lewandowski, Solid State Ionics, 28 (1988) 1338.

10 L. M. Nunes, A. G. Souza and R. F. Farias, J. Alloy Compd., 15 (2000) 320.