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CHARACTERIZATION OF THE HYDROGENATED SPECIES IN $Li_2Ti_4O_9.nH_2O$ BY ISOTHERMAL WEIGHT-CHANGE DETERMINATION

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ABSTRACT

Isothermal weight-change determination was used to characterize the nature of the hydrogenated species (OH^-, H_2O, H_3O^+) present in $Li_2Ti_4O_9.H_2O$.

This product contains two OH^- groups and five H_2O molecules per unit formula and may be formulated as $Li_2Ti_4(OH)_2O_8.5H_2O$.

INTRODUCTION

A microcrystalline phase with the formula $Li_2Ti_4O_9.nH_2O$ has recently been synthetized by reaction of hydrated titania gel in TiO_2-Li_2O-H_2O system [1].

This phase resembles an analogous compound ($K_2Ti_4O_9.3H_2O$) synthetized by hydrothermal treatment of the corresponding anhydrous form [2]. Alkali-tetratitanates are characterized by a structure of low compactness and can be employed in catalysis and chemical storage of energy [3]. The anhydrous $Li_2Ti_4O_9$ is well known [4], whereas the corresponding hydrated phase has not been synthetized. Moreover, the water molecule content of $Li_2Ti_4O_9.nH_2O$ is higher than that reported for $K_2Ti_4O_9.3H_2O$.

This paper deals with the characterization of the hydrogenated species (OH^-, H_3O^+ and H_2O) present in $Li_2Ti_4O_9.nH_2O$ with a view to the possible employment of this phase in catalysis, ion exchange or the chemical storage of energy.

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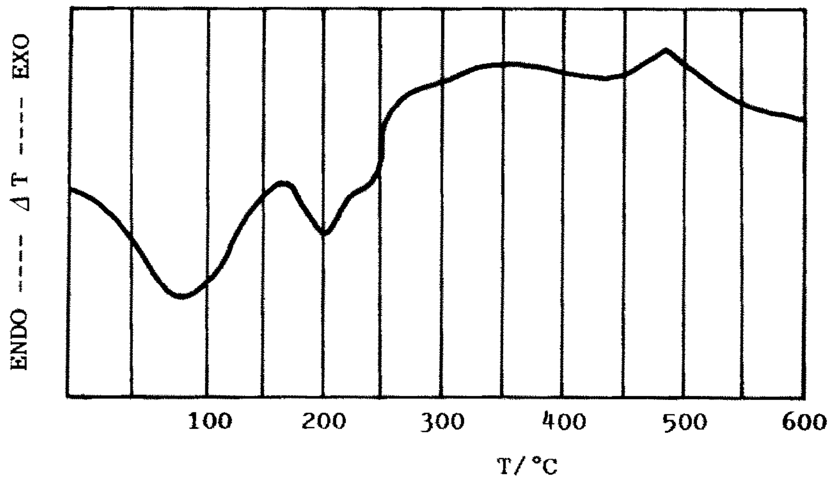

Fig. 1. DTA curve of $Li_2Ti_4O_9.nH_2O$ compound.

EXPERIMENTAL

A stock of $Li_2Ti_4O_9.nH_2O$ was prepared by hydrothermal treatment at 110 °C of hydrated titania gel in LiOH solution with a molar ratio Li/(Li+Ti) equal to 0.5 and a reaction time of a week, as previously described [1].

The specimens were dried in air and subjected to a heating cycle with a simultaneous DTA and TG apparatus. Each cycle was performed on 20 mg of sample at 10 °C min^{-1}.

Isothermal weight-change determination is performed by heating specimen to the temperature programmed for the isotherm, followed by a stop long enough to assure a constant weight, and by a subsequent heating that completes the dehydration associated with the specimen. During the first step a certain weight loss of H_2O moles was determined, H_2O(BT), while the weight loss following the isotherm was H_2O(AT).

$Li_2Ti_4O_9.nH_2O$ was also equilibrated with solutions of HCl $1x10^{-2}$ mol dm^{-3} by stirring a slurry $2x10^{-3}$ moles of the sample for 24 h.

RESULTS AND DISCUSSION

The DTA curve of $Li_2Ti_4O_9.nH_2O$ shows three endothermic effects at 75, 200, and 230 °C, and an exothermic effect at 480 °C. H_2O is completely removed at about 500 °C (see Fig.1).

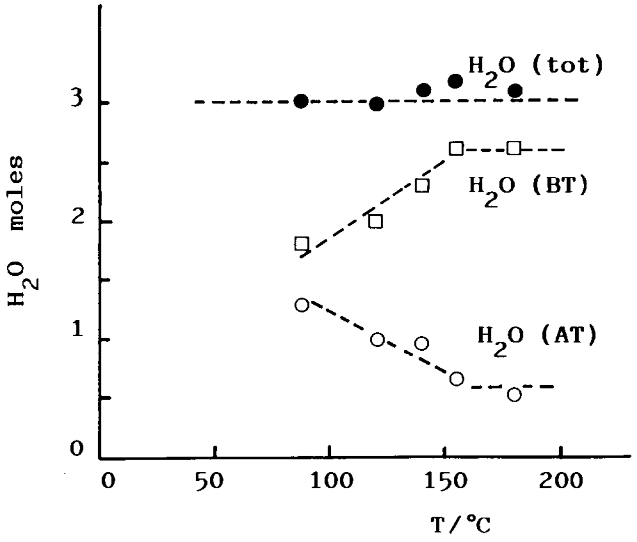

Fig. 2. Moles of H_2O per mole of Li^+ as a function of the isotherm temperature.

To discriminate the nature of the hydrogenated species related to the sample, a series of heating cycles with isotherms of 80 to 180 °C was performed. The following H_2O moles per mole of Li^+ were measured for each isotherm (see Fig.2): the total weight loss, H_2O(tot), the weight loss after the isotherm, H_2O(BT), and the difference H_2O(AT) = H_2O(tot) - H_2O(BT).

In the range 80 to 150 °C H_2O(BT) increases with decreasing H_2O(AT), while in the range 150 to 180 °C a constant value for both H_2O(AT) and H_2O(BT) can be observed.

This behaviour has suggested two different hydrogenated species: H_2O, released with isotherm up to 150 °C, and OH^- groups above 180 °C.

This deduction has been confirmed by infrared analysis. Specimens cooled from isotherms between 80 and 150 °C show both OH^- and H_2O absorption bands, while those from isotherms 150 and 180 °C show OH^- vibration bands only.

The data in Fig. 2 give the following formulation for the sample:

$Li_2Ti_4(OH)_2O_8.5H_2O$

The X-ray powder diffraction pattern of the sample remains almost unchanged up to 200 °C, giving rise to an amorphous solid at 250 °C. Crystallization then takes place at 450 °C, due to the formation of TiO_2 (anatase) and Li_2TiO_3 [5].

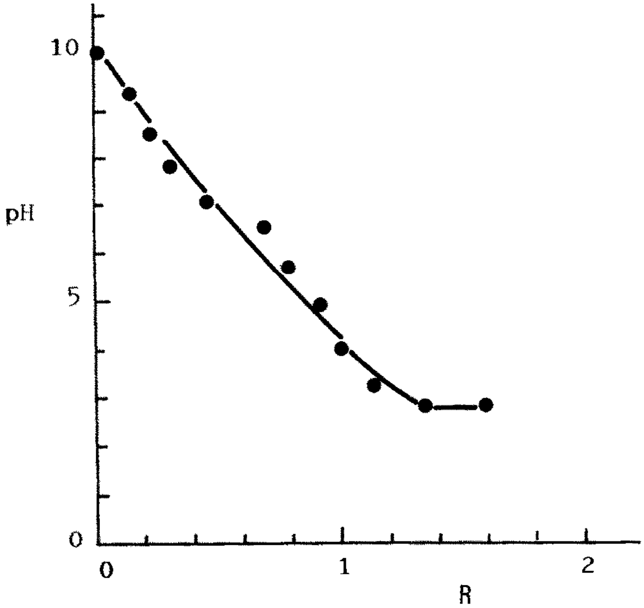

Fig. 3. Equilibrium pH values obtained after addition of H_3O^+ to $Li_2Ti_4O_9.nH_2O$ in suspension. R = moles of H_3O^+ added per mole of Li^+ in the solid.

Fig. 3 gives the pH values measured on suspensions of the sample equilibrated with solutions of HCl $1x10^{-2}$ mol dm^{-3}. The progressive diminution of pH with the increasing addition of HCl suggests no interaction between the H_3O^+ and OH^- groups. On the other hand, the bend in the curve where R=1 (R represents the moles of H_3O^+ added per mole of Li^+ in the solid) may be explained by the following reaction:

$$Li_2Ti_4(OH)_2O_8.mH_2O + 2H_3O^+ \longrightarrow H_2Ti_4(OH)_2O_8.m'H_2O + 2Li^+$$

This reaction has been confirmed by the nature of the calcination products of the acid-form of Li tetratitanate hydrate; after treatment at 900 °C, in fact, only presence of the two polymorphic forms of TiO_2 (anatase and rutile) [6] and absence of Li containing phases were found.

CONCLUSIONS

The characterization of recently synthetized lithium tetratitanate hydrate has furnished the following formulation: $Li_2Ti_4(OH)_2O_8.5H_2O$.

The product appears very promising for applications in the field of ionic exchange and solid electrolytes, with particular reference to the protonic conductors.

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