

The effect of chemical modifications of 1-D alkali titanate nanomaterials on their stability in acidic aqueous suspension

P.M.Jardim^{(1)*}, B.A.Marinkovic⁽¹⁾, J.M. Andrade⁽¹⁾, F.Rizzo⁽¹⁾, M. A.S. de Abreu⁽²⁾ and E. Morgado Jr.⁽²⁾

(1) DCMM, Pontifícia Universidade Católica do Rio de Janeiro, e-mail: paula@puc-rio.br

(2) PETROBRAS S.A. / CENPES, Research & Development Centre

* Corresponding author.

Abstract – The acidic stability of chemically modified 1-D nanomaterials synthesized by alkali hydrothermal method was evaluated. The results suggested that either ion-exchanged cations or structurally inserted metals can affect the acidic stability of these materials. Moreover, acidic aging of 1-D titanate nanomaterials turned out to be an interesting route for synthesizing TiO₂ nanoparticles whose crystal structure (anatase and/or rutile) can be controlled by chemical modification of the titanate precursor.

In 1998 Kasuga et al [1] reported an innovative method for the production of TiO₂-derived 1-D nanomaterials (nanotubes and nanowires) by a hydrothermal alkali treatment without using any templates. This simple soft-chemistry synthesis method motivated intensive research in the recent years. Structural and chemical fundamental studies on this class of materials pointed out that these 1-D nanometric forms actually present layered titanate crystal structure with the general formula A₂Ti_nO_{2n+1}·nH₂O, where A is a positively charged cation, usually Na⁺ and/or H⁺, sited, commonly together with water molecules, within the interlayers in order to fulfill charge balance with the negatively charged layers. Such a layered crystal structure allied with nanometric dimensions of these 1-D forms opens path for chemically controlled modifications of physical properties through exchange of interlayer cations. These materials show promise for applications such as hydrogen sensors, adsorbents, photocatalysts, mesoporous catalyst supports, solar cell photosensitizers, ion-exchange materials, new generation electrodes for lithium batteries and electrocatalysts. In many of these applications, titanate 1-D nanomaterials can be exposed to chemically aggressive media. Therefore, in the present work we studied the effect of chemical modifications of these nanomaterials on their stability in acidic aqueous suspension. Two chemical modification approaches were used: ion exchange of Na⁺ with different cations and also the introduction of Zr⁴⁺ partially substituting for Ti⁴⁺ in the structure, when using rutile sand as the precursor, which contains ZrSiO₄ as an impurity.

The 1-D nanomaterials were hydrothermally synthesized from a 10M NaOH solution using commercial anatase and natural rutile sand as TiO₂ precursors. The as-synthesized Na⁺ rich product obtained from anatase was ion-exchanged with H⁺, Co²⁺ and Fe³⁺. Each product was submitted to acidic aging in a 0.1M solution of sulfuric acid during 28 days. The samples, before and after acidic aging, were analyzed by X-ray diffraction and transmission electron microscopy. After acidic aging the samples transformed partially or completely into anatase and/or rutile nanoparticles. The sample obtained using natural rutile sand as precursor showed the best stability (fig.1) followed by the sample ion exchanged with Fe³⁺, both only partially converted to rutile nanoparticles. All the other samples completely transformed into TiO₂ nanoparticles after acidic treatment. The treatment of H⁺ rich titanate resulted mainly in anatase nanoparticles (fig. 2) with a smaller amount of rutile nanoparticles while Na⁺ and Co²⁺ samples resulted only in rutile nanoparticles. These results suggested that chemical modification of 1-D titanates nanomaterials affects the acidic stability of these materials. The replacement of Ti⁴⁺ in the structure (in this case by Zr⁴⁺) was more effective than the ion-exchange of interlayer cations. Moreover, the acidic aging of 1-D titanate nanomaterials was found to be a promising route for synthesizing TiO₂ nanoparticles whose crystal size and structure (anatase and/or rutile) can be controlled by managing chemical modifications on the as-synthesized sodium titanate precursor.

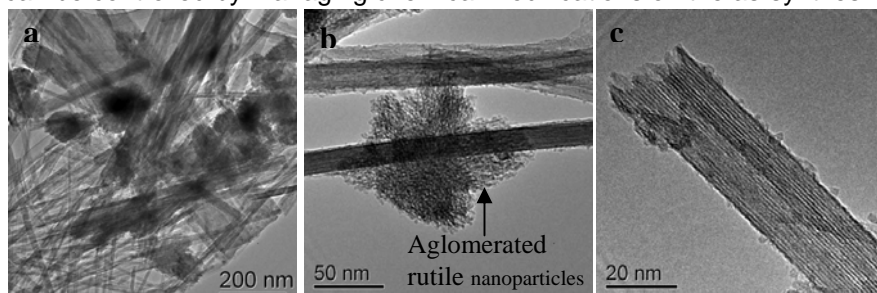


Fig. 1: Sample synthesized using rutile sand as precursor after acidic aging.

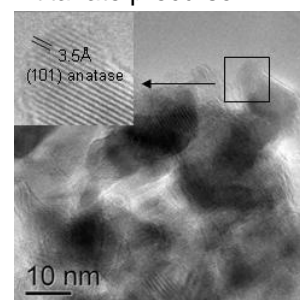


Fig. 2: H⁺ rich sample after acidic aging.