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A study on the structure/phase transformation of titanate nanotubes synthesized at various hydrothermal temperatures.

ABSTRACT

A conversion from commercial titania (TiO_2) nanoparticles to nanotubes was achieved by hydrothermal method with 10M NaOH solution at various reaction temperatures ranging from 70 to 150 C over 48 h. Most of intercalated sodium in as-synthesized titanate nanotubes was removed by washing with 0.1 M HCl solution for 1 h. The samples were then dried at room temperature and annealed at 300, 400, 500, and 600 C in air for 1 h. With increasing reaction temperature, the morphology varied from spherical particles to two-dimensional nanosheets to one-dimensional nanotubes. At 110 C, nanosheets transformed to tube-like structure. The reaction temperature is a key factor in determining the overall aspect ratio of the tubular material. X-ray diffraction supports the structural transformation indicating the gradual changes in the phase and crystallinity of the synthesized powder. Tubular structure collapsed when annealed at 600 C and converted to anatase phase totally. O 1s peak is found built-up of sub-peaks of H_2O , -OH, Ti-O. Annealing at 600 C reduces the peak intensity of H_2O (531.0eV) and -OH, while that of Ti-O increases. It is found that annealing removes the chemical bonds such as H_2O , -OH from the titanate and also converts the bonded states of titanate to that of titania.

1. Introduction

After the innovative work of Kasuga et al. [1], titanium dioxide and/or titanate nanotubes (TNT) with large specific surface area and pore volume have gained promising and important prospect due to their fascinating microstructures and excellent properties. High-quality TNT can be synthesized from the crystalline titania (TiO_2) particles (anatase, rutile or mixed phase) and highly concentrated sodium hydroxide (NaOH) solution using hydrothermal method. The key parameter affecting crystallinity and scroll structure [1-5] is the content of NaOH. The reported experiments [5-

10] based upon the “hydrolysis of titania particles using NaOH solution” revealed that nanorubular structures containing ‘Ti-O framework’ similar to TiO_2 could indeed be formed. However, it is realized that substantial amount of sodium (Na) gets incorporated in these nanotubes. The walls of these nanotubular are believed to have layered structure. Although the structure is similar to sodium titanates [11,12], overall crystallinity is poor due to incorporated sodium. Evidently, the presence of sodium in such nano-sized titania material is expected to deteriorate/modify properties rendering lower efficiency of material for applications. Many groups tried to modify the process or to analyze the structure of the resulting titania or TNT. The formation mechanism and the true composition of TNT are still under debate. Additionally, the issues like structure stability and corresponding crystalline phases at various NaOH concentrations, and calcination temperatures remain to be addressed from the point of the view of practical application [1,4.5.13—15].

Discrepancies related to different crystal structures and compositions, structure transformation and treatment duration clearly demonstrate the need for further investigation on this subject. For example, the study of thermal decomposition of TNT may lead to important conclusions on its original crystal structure and its behavior upon heat treatment [2,11,16,17]. Therefore, the present work focuses on structure and phase transformation of titanate by: (i) step-by-step synthesis, (ii) sodium removal by acid washing and (iii) heat treatment during hydrothermal process. Detailed and systematic structural and chemical characterizations are presented. Additionally, it is intended to provide information on the thermal stability via sodium removal of synthesized products.