# Titanate Nanotubes as Futuristic Catalyst Support Material

**Venkataraman Vishwanathan, Lucky Sikhwivhilu**

***Abstract:** Titanate Nanotubes (TNT) were synthesized by aging commercial titanium dioxide ($TiO_2$ - Degussa P25) with an alkali (KOH) solution at different time intervals. The prepared materials were investigated for their surface composition and textural behaviour by X-ray powder diffraction (XRD), Raman spectroscopy, Gas ($N_2$ and $CO_2$) adsorption measurements, and Transmission electron microscopy (TEM). The X-ray diffraction spectra revealed the decrease in the crystalline nature of the materials decreased by exposing them for a longer duration in the base solution. Raman spectra results showed that ageing time affected the structural properties. The specific surface area and the pore size of the newly synthesised materials were affected by the ageing process. The TEM images showed the influence of ageing during the formation of titanate nanotubes. HRTEM revealed that Pd particle sizes of <1 nm was present inside the tubes.*

***Keywords:** Nanotubular; Morphology; Structural Composition; Catalyst Support.*

## I. INTRODUCTION

The structural composition and morphology of various carbon nanotubes and nanofibers have been reported. Titanate nanotubes (TNTs) derived from titanium dioxide have interesting behaviour in surface chemistry in terms of structural changes and morphological differences [1]. Several applications of titanates nanotubes in various industrial products have been reported [2,3]. The importance of tubular form of titanate to be used as a suitable catalytic support material is emphasised further due to its high surface area, thermal stability, and longer life during the course of the reaction [4]. Conventionally sol-gel approach is employed to prepare titanate nanotubes used to synthesize $TiO_2$ based nanotubes using various organic and inorganic templates [5,6]. These preparatory routes are and provide more pure and homogeneous products [7,8,9]. In all these methods, the difficulty lies in the removal of template after the reaction. Most of the reports have indicated that the treatment with an acid may be a crucial step [10,11]. In our investigation titanate nanotubes were synthesized by using a base (KOH) solution and exposing them at two different time intervals.

The aim of the study was to synthesise the tubular form of titanium dioxide through a simple methodology and to understand their structural composition and surface morphology from the catalyst support point of view using different characterisation techniques techniques.

## II. EXPERIMENTAL

Titanate nanotubes (TNTs) were synthesied by treating an alkali solution of KOH (18 M) with a commercially available titania ($TiO_2$) (Degussa P-25) sample. The mixture (Titania + KOH) was placed in a teflon container and heated at 120ºC for 20 h and cooled to room temperature. Two sets of TNT samples were prepared based on two ageing intervals (0 and 61 days). After ageing, the two samples were thoroughly washed with water to remove the base KOH. They were then dried and designated as **$TiO_2$-B and $TiO_2$-C** according to the ageing intervals 0 and 61 days respectively. To compare the synthetic samples ($TiO_2$-B and -C) with Degussa P-25 ($TiO_2$) sample, the as-received sample was made into a paste by adding water into it. The dried material was crushed to a desired size, and designated as **$TiO_2$-A**. To study the influence of metal present inside TNT, Pd metal (1 wt%) was added over $TiO_2$-C by impregnating $Pd(CH_3COO)_2$. The sample was dried, sieved and designated as **CAT-C** (i.e. Pd (1wt%) / $TiO_2$-C).

## III. CHARACTERISATION STUDY

X-ray diffraction (XRD) profiles of all the materials were studied using recorded on a Phillips PW1830 Diffractometer. Raman spectra of the $TiO_2$ samples were investigated by Jobin-Yvon T64000 spectrometer under a triple subtractive mode. Specific surface area of the samples was determined by the $N_2$ adsorption and desorption measurements at -195ºC using an ASAP 2010 porosimeter. The basicity of the samples was measured through adsorption of an acidic molecule ($CO_2$) at 27ºC. Transmission electron microscopy (JEOL 100S microscope) was used to understand the morphological features of all the samples The experimental procedure of some of the techniques used were reported earlier [12].

## IV. RESULTS AND DISCUSSION

The synthesis of nanotubular titanate materials from NaOH have been reported earlier [13,14]. Studies made earlier on the synthesise of nanotubes under base condition have led to sheet like structural formation of titanate nanotubes [15]. However, using a higher concentration of KOH and ageing for a period of time has shown successful formation of nanotubular titanate (as described in Section 2).

Manuscript received on October 07, 2021.
Revised Manuscript received on October 13, 2021.
Manuscript published on October 30, 2021.

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### A. X-ray diffraction (XRD) and Raman analysis

The XRD profiles of $TiO_2$ materials (-A, -B and -C) are shown in Fig.1. The commercial titania ($TiO_2$-A) showed a high crystallinity consisting of a mixture of less rutile and more of anatase phases. However, the material which was only soaked in KOH solution ($TiO_2$-B) showed amorphous nature with high degree of anatase phase. This indicates that the rutile phase can be reduced or eliminated from the $TiO_2$ sample by a simple treatment with a base solution The diffractogram of $TiO_2$-C showed broad peaks with low intensities. This suggest that the sample has a poor crystallinity and remains amorphous after ageing for a period of 61 days.

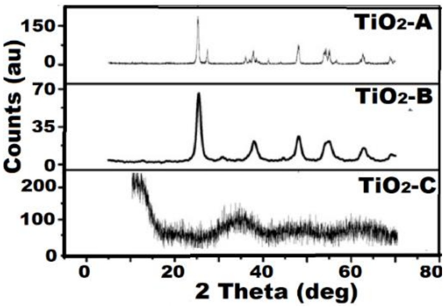

**Fig.1. XRD profiles of $TiO_2$-A, -B, and -C.**

The Raman spectra of $TiO_2$-A and -B samples are shown in Fig.2. Broadening of the peak observed for the sample $TiO_2$-A reflects the presence of smaller crystallites. The sharp bands appeared in $TiO_2$-B reflects the presence of larger crystallites when $TiO_2$-A was treated with KOH solution without ageing. The formation of larger crystallites may be due to the rapid reaction of smaller crystallites with the KOH solution before ageing. The Raman spectrum of sample $TiO_2$-C (Fig. 2, inset) shows multiple broad peaks implying the poor crystallinity of the sample. This confirms further with XRD data. The peaks at 188, 271, 441 and 652 $cm^{-}1$ show the existence of titanate species [16,17]. From the EDX investigation, it was found that of $TiO_2$-C sample has 19% potassium ions left after washing with water. This suggests that the titanate nanotubes may have a potassium titanate structure [18].

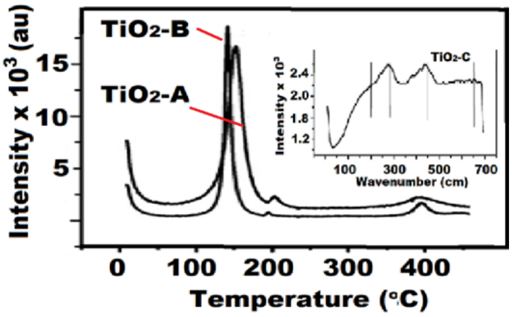

**Fig.2. Raman spectra of $TiO_2$-A &-B and the inset $TiO_2$-C.**

### B. Surface area analysis

The surface properties of the samples are reported in Table 1. The surface area values of samples $TiO_2$-A and -B samples has not varied much. However, ageing for 61 days showed a low surface area of 36 $m^2/g$ ($TiO_2$-C) as compared samples $TiO_2$-A and -B. This shows soaking $TiO_2$-A in KOH solution for a longer period transform the smaller crystallite of anatase particles into larger crystallites. The surface area has further decreased after impregnation Pd metal over $TiO_2$-C to a value 25 $m^2/g$. This shows that the palladium particles must have entered the pores of titania. The average pore diameter of $TiO_2$-A & -B are very similar (Table 1). However, $TiO_2$-C and Pd/$TiO_2$-Cs samples showed a higher value. The pH values too showed an increase with ageing time resulting in high level of basicity.

**Table 1. Surface properties of both commercial and synthetic $TiO_2$.**

| Sample | Ageing interval (days) | Surface area ($m^2g^{-1}$) | Pore size (nm) | pH |
|---|---|---|---|---|
| $TiO_2$-A | As received | 50 | 5.9 | - |
| $TiO_2$-B | 0 | 52 | 5.4 | 7.76 |
| $TiO_2$-C | 61 | 36 | 8.9 | 10.50 |
| Pd (1wt%) /$TiO_2$-C | - | 25 | 9.4 | - |

### C. Temperature programmed desorption (TPD) studies CO2

TPD analysis of $CO_2$ samples were studied to determine the the basic sites and their strength. TPD profiles of $TiO_2$-A, -B and -C are shown in Fig.3. A significant difference in surface basicity was observed in the case of all three samples. The $TiO_2$-C sample which was aged for a longer duration in KOH solution showed the largest $CO_2$ desorption areas.

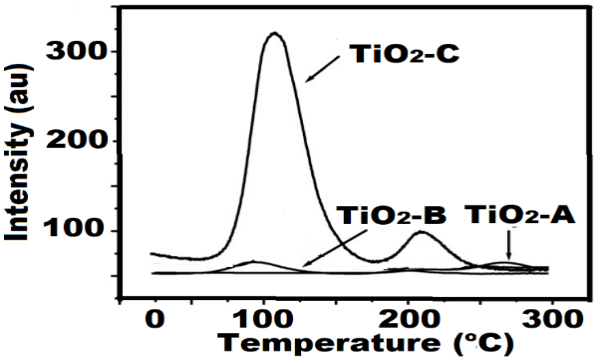

**Fig.3. TPD curves profiles of samples $TiO_2$-A, -B & -C.**

The occurrence of the desorption peaks below 270ºC attributes to the transformation of few weak basic sites into medium basic sites on the material.

### D. Electron Microscopy studies

The surface morphology of the samples was analysed by TEM (Fig.4). The sample $TiO_2$-A shows agglomeration of smaller crystallites of anatase particles having with an average diameter of

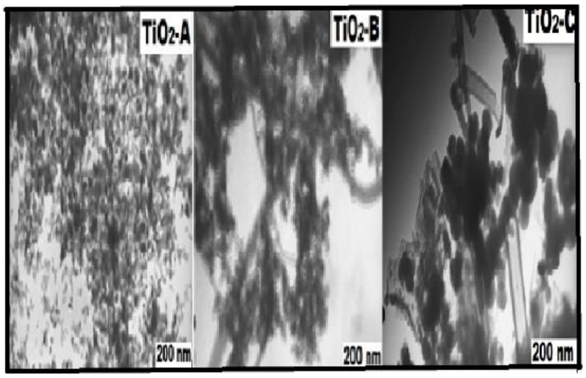

**Fig. 4. TEM profiles of $TiO_2$-A, -B, and -C samples.**

75 nm. $TiO_2$-B shows a random distribution of 100% nanotubes in a diameter range between 8 and 11 nm and are one hundred to several hundred nanometres in length. The nanotubes appear to be thin walled and open-ended. While $TiO_2$-C shows the presence lesser tubes with less crystallinity. The presence of low crystallinity suggests that the nanotubes get dissolved with longer contact time in KOH solution and make the material more amorphous The presence of tube-like structures may be sheets formed at first which then transformed into tube formation [19]. High resolution TEM of CAT-C (Fig. 5) shows that the nanotubes are aligned in a parallel mode after the addition of Pd particles over $TiO_2$-A.

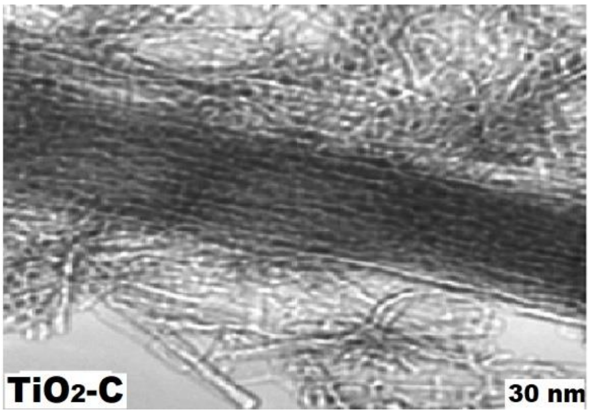

**Fig.5. High resolution TEM image of TiO2-C impregnated with 1 wt% Pd (i.e. CAT-C).**

Further, it revealed that the titanate nanotubes are multi-walled and present in bundles. This agrees well the literature [14]. The formation of nanotubes with acid treatment and the formation mechanism is not understood well [20]. The formation of nanotubes is largely depend on the disordered intermediate phase while in contact with KOH solution [13]. Based on the present observation, a reaction between $TiO_2$ and KOH will form Ti–O–K and Ti–OH bonds as a primary step. On increasing the contact time in KOH solution, the material $TiO_2$-A rolls into nanotubes. The basicity of the solution plays an important role, and the nanotubes are largely formed below pH value of 10. Beyond this, the nanotubes are unstable and become amorphous with ageing time [20].

## V. CONCLUSIONS

Commercial titania ($TiO_2$) sample (Degussa P-25) was used to synthesise titanate Nanotubes (TNT) by treating with a base KOH solution at two different ageing intervals. The contact time (i.e., ageing) of $TiO_2$ in a concentrated KOH solution plays an important role in the formation of titanate nanotubes (TNTs). It was observed that ageing for a longer duration ($TiO_2$-C) showed the formation of a well-developed tubular structure with less crystallinity. However, in the absence of ageing, nanosheet type of material with a high degree of crystallinity was formed. It was also noticed that the longer duration of contact time of $TiO_2$ in KOH solution had a significant influence on both surface area as well as on the pore diameter of titanate nanotubes. TEM and HRTEM images showed the influence of ageing time in the formation of tubular structure of TNT and the presence of Pd particle sizes of <1 nm present inside the tubes, respectively.

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