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High temperature stability of nanocrystalline anatase powders prepared by chemical vapour synthesis under varying process parameters

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ABSTRACT

Systematic variation in the high temperature stability of nanocrystalline anatase powders prepared by chemical vapour synthesis (CVS) using titanium (IV) isopropoxide under varying flow rates of oxygen and helium was obtained by progressively shifting the decomposition product from C_3H_6 to CO_2. The as-synthesised powders were characterised by high temperature X-ray diffraction (HTXRD), simultaneous thermo-gravimetric analyses (STA), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM). It was observed that the anatase to rutile transformation temperature progressively increased for samples synthesised at higher O_2/He flow rate ratios. The improved anatase stability was attributed to the presence of incorporated carbon within the titania structure and confirmed by a high temperature carbon desorption peak.

1. Introduction

Nanocrystalline titania (TiO_2) has emerged as an important oxide ceramic material by virtue of its novel physical, chemical and electrical properties. It finds application in various fields that include photo-catalysis, solar cell applications, gas sensing, nitrogen fixation etc. [1–4]. Titania exists in three different crystallographic modifications: rutile, anatase and brookite. In the conventional form, rutile is the thermodynamically stable phase while anatase and brookite are metastable and transform to rutile on heating. It is a well-established fact that the property of titania is dependent on the phase content [1]. Rutile has a high absorption coefficient in the UV range and finds use primarily as pigments and paints. On the other hand, anatase has higher chemical/catalytic activity and functional value. For instance, nanocrystalline anatase TiO_2 having high surface area is an essential phase in lithium batteries [4]. It has been shown that at room temperature anatase becomes thermodynamically stable only when the crystallite sizes are lower than about 14 nm [5,6]. However, on heating to higher temperatures, nanocystalline anatase has a high tendency to grow and transforms irreversibly to the stable rutile form [7,8]. The temperature of anatase to rutile transformation depends on the initial (anatase) particle size [8], synthesis route [9,10] and impurities [11,12]. For micron sized particles the transformation temperature is about 600–800 °C [13]. On the other hand, nanosized anatase particles transform to rutile at much lower temperatures because of the high specific surface area which act as nucleation sites for the transformation [8].

Therefore, it is of interest to develop methods that can either stabilise the anatase particles to higher temperatures or increase the anatase to rutile transformation temperature. The most popular way to increase the transformation temperature of the anatase particles is to dope them with other oxides like zirconia and alumina [14,15]. One of the major disadvantages of this approach is that the as-prepared samples are mostly amorphous and any heat treatment results in the reduction of surface area and growth of particles that affect its catalytic properties adversely. At the same time, these metal oxides form impurity phases (like Al_2TiO_5, $NiTiO_3$) at higher temperatures. It has been shown that addition of urea during the sol–gel preparation results in anatase particles that can remain stable up to 800 °C on annealing for 2 h [16]. Recently, it has been observed that the synthesis route has an effect on the anatase-rutile transformation. Sun et al. [9] synthesised nanocrystalline anatase by chemical vapour deposition and reported a transformation temperature of 800 °C on annealing for 1 h.

There are few reports on the effect of process parameters on the phase composition of titania powders prepared by gas phase synthesis. During flame synthesis an increase in the precursor flow rate in the reactor resulted in higher rutile content in the resultant powder [11,17]. Higher rutile contents were also observed in case of

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powders synthesised at higher hotwall temperatures and increased oxygen flow rates during CVS [18]. However, to the best of our knowledge there is no report on the effect of gas flow rates on the high temperature phase stability of titania. In this study nanocrystalline anatase titania was prepared by a CVS process [18–23] by systematically varying the gas flow rates and its effect on the phase stability was studied.

2. Experimental

Nanocrystalline titania was synthesised by a chemical vapour synthesis process, using tetra titanium iso-propoxide (TTIP) as a precursor. TTIP was fed into a hotwall reactor through a bubbler with helium as a carrier gas. Oxygen was fed into the reactor through a separate line to ensure effective decomposition and formation of TiO_2. Flow of oxygen and helium were controlled by MKS mass flow controllers. The synthesised powders were collected using a thermophoretic collector. Details about the CVS equipment and the experimental set up can be found elsewhere [19]. Synthesis of the nanocrystalline titania powders was carried out under different oxygen to helium gas flow rate ratios.

The as-synthesised powders were characterised by high temperature X-ray diffraction (Brucker D8) in the 2θ range of 20–32° in a snapshot mode. Each snapshot was collected for an exposure time of 60 s while samples were heated at the rate of 10 °C min^{-1}. Therefore, each such pattern represented an average state of the sample within the exposure time of 60 s during which the sample temperature increased by 10 °C.

A commercial package TOPAS®, was used to analyse the obtained XRD patterns. The background was fitted with a fifth order polynomial expression while fundamental parameter peak type was used for peak profile fitting. Phase composition of anatase and rutile were estimated from the integrated intensities of the corresponding anatase and rutile peaks at 2θ values of 25.4° and 27.6°, respectively, by using the Eq. (1).

$$F_A = 100 - \left(\frac{1}{(1 + 0.8 \times I_A(1\,0\,1))/(I_R(1\,1\,0))}\right) 100 \quad (1)$$

where, $I_A(1\,0\,1)$ is the intensity of (1 0 1) peak of anatase, $I_R(1\,1\,0)$ is the intensity of (1 1 0) peak of rutile and F_A is the fraction of anatase.

Simultaneous thermal analysis of powder samples were carried out in a NETZSCH STA 449 °C machine attached to a quadrupole mass spectrometer. Measurements were carried out under oxygen atmosphere with a heating rate of 10 °C min^{-1}.

The synthesised powders were also characterised by high resolution transmission electron microscopy (HRTEM), nitrogen adsorption using the Brunauer, Emmett and Teller (BET) method [24], X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR).

3. Results and discussion

Table 1 lists the XRD crystallite sizes and specific surface areas of the resultant powders synthesised with varying O_2/He flow rate ratios at constant O_2 flow rates of 1000 and 250 sccm. It was observed that in all cases the anatase crystallite size varied between 5 and 7 nm. The specific surface areas in all the cases were nearly the same keeping the inherent experimental errors in the BET approach of estimating the specific surface area. The particle sizes estimated from the specific surface areas varied between 6 and 9 nm which were very close to the crystallite sizes obtained from XRD. This indicated that particles in all the cases were essentially single crystals and therefore, no hard agglomerates were present in the samples. This ruled out the possibility of the size and degree of agglomeration playing a role in the anatase to rutile transformation in case of the powder samples.

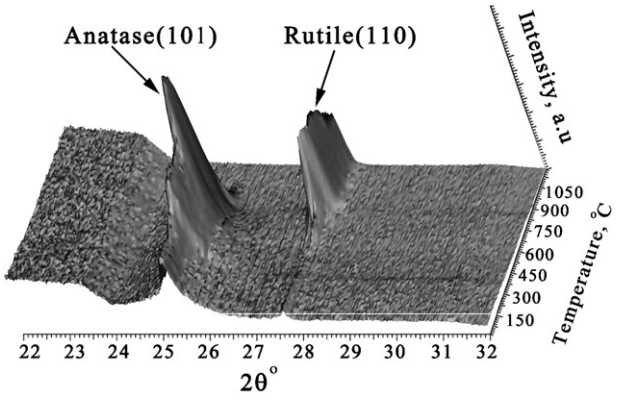

Fig. 1. High temperature X-ray diffraction pattern of a sample synthesised with an O_2/He flow rate ratio of 1.33 showed initial sharpening (hard to see in this figure) of the anatase (1 0 1) peak and appearance and growth of the rutile (1 1 0) peak at the expense of the anatase peak at higher temperatures.

The HTXRD patterns of different samples revealed that at room temperature the samples contained little or no rutile phase as can be observed from Figs. 1 and 2. However, as the temperature was raised above 400 °C the anatase (1 1 0) peak at a 2θ value of 25.4° became sharper indicative of crystallite growth. As the temperature approached 600–700 °C the rutile (1 0 1) peak at 2θ of 27.6° appeared. With further increase in temperature the integrated intensity of the rutile peak increased while at the same time the integrated intensity of the anatase peak kept decreasing till it finally vanished in the vicinity of 800–950 °C. It was observed from the HTXRD measurements that in all cases the anatase crystallites grew initially to about 15–20 nm, before transforming to the stable rutile phase in the temperature range of 700–900 °C. However, the actual transformation temperature ranges for samples synthesised under different oxygen and helium flow rates during chemical vapour synthesis were different. It was seen that the transformation temperature was higher for the samples synthesised with higher O_2/He flow rate ratio, indicating a higher stability of the anatase phase. Fig. 3 depicts the XRD patterns at 800 °C for the samples synthesised at different O_2/He flow rate ratios of 0.66, 1.33 and 2.66. From the respective peak intensities in Fig. 3, it can be seen that a higher O_2/He flow rate ratio during CVS resulted in a progressively larger fraction of anatase at 800 °C.

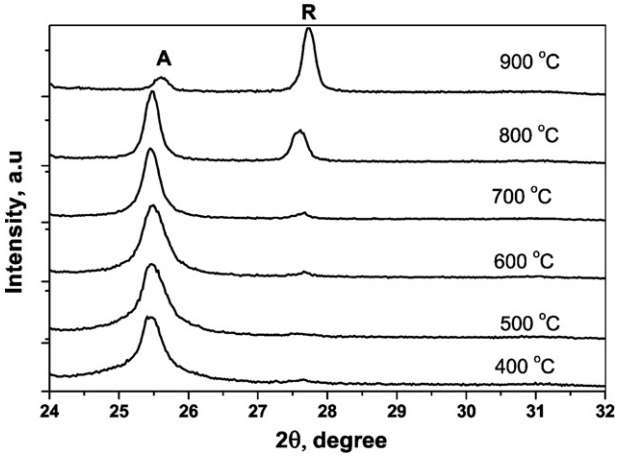

Fig. 2. XRD patterns of the a sample (synthesised at O_2/He flow rate ratio of 1.33) at different temperatures showed that on heating initially the anatase peak (24.5°, A – anatase (1 0 1) peak) becomes sharper while above 600 °C the rutile peak (27.6°, R – rutile (1 1 0) peak) appears and grows at the expense of the anatase peak.