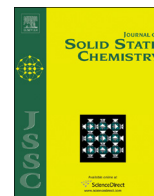




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Comparative study of phase transition and textural changes upon calcination of two commercial titania samples: A pure anatase and a mixed anatase-rutile

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ABSTRACT

The effect of calcination temperature and time on structural and textural changes of two commercial TiO₂ samples (pure anatase and a mixture of anatase and rutile) has been investigated using N₂ physisorption, ex-situ and in-situ X-ray powder diffraction, differential scanning calorimetry and UV–vis diffuse reflectance spectroscopy.

The increase of the calcination temperature (up to 700 °C) and time (up to 8 h) causes only textural changes in the pure anatase, whereas a transformation of the anatase to rutile takes place, in addition, in the mixed titania (containing anatase and rutile).

The textural changes observed in pure anatase sample were attributed to solid state diffusion leading to an increase in the size of anatase nanocrystals, through sintering. Thus, the mean pore diameter shifts to higher values and the pore volume and specific surface area decrease. The successful application of the Johnson–Mehl–Avrami–Kolmogorov model in the kinetic data concerning the pure anatase indicates a mass transfer control of sintering process.

Similar textural changes were also observed upon calcination of the sample containing anatase and rutile. In this case not only sintering but the anatase to rutile transformation contributes also to the textural changes. Kinetic analysis showed that the rutile nanocrystals in the mixed titania served as seed for by-passing the high energy barrier nucleation step allowing/facilitating thus the anatase to rutile transformation.

A fine control of the anatase to rutile ratio and thus of energy-gap and the population of hetero-junctions may be obtained by adjusting the calcination temperature and time.

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1. Introduction

Titanium dioxide is a widely investigated material in the field of catalysis [1, 2]. Anatase, rutile, and brookite are three polymorphs of TiO₂ which differ only in arrangement of their [TiO₆]²⁻ octahedra; anatase (tetragonal) consists of octahedra sharing vertices; in rutile (tetragonal) octahedra are connected by edges, and in brookite (orthorhombic) both edges and vertices are connected. Rutile is the thermodynamically stable phase, while anatase and brookite are both metastable, transformed to rutile under heat treatment at temperatures typically ranging between 600–

700 °C [3]. However, anatase has been found to be the majority product of industrial sol-gel and aerosol syntheses of titanium dioxide [4]. Moreover, anatase is common in samples at nanoscale [5–7]. The surface enthalpies of anatase and rutile are sufficiently different. Therefore, a crossover in thermodynamic stability can occur which makes anatase the stable phase at nanoscale [7, 8].

TiO₂ is believed to be the most promising photocatalyst because of its superior photoreactivity, nontoxicity, long-term stability, and low price. The photocatalytic activity of TiO₂ depends on various parameters, including crystallinity, impurities, surface area, and density of surface hydroxyl groups; however, the most significant factor seems to be its crystal form [2, 9].

TiO₂ is usually used as a photocatalyst in two crystal structures: anatase and rutile. Anatase generally exhibits much higher activity than rutile. However, the activity of P25 (Degussa), consisting of

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anatase and rutile (~80/20 w/w), exceeds that of pure anatase in several reactions. Thus, P25 is frequently used as a benchmark for photocatalysts [9].

On the other hand, it is well known that TiO₂ in the form of anatase presents excellent supporting properties for several catalytic systems involved in important thermo-catalytic processes; characteristic examples are NO_x reduction with NH₃ [10–12] and oil hydrodesulphurization [13–15]. In these cases the major disadvantage of the titania support is its relatively low thermal stability resulting to the transformation of anatase to rutile, which is accompanied by dramatic reduction of the specific surface area and pore volume.

It has been reported several times that the anatase to rutile transformation depends on the size of nanocrystals, impurities, reaction atmosphere and synthesis conditions [4, 8, 16–22]. For example, the synthesis of titanium dioxide leads in anatase nanocrystals which are transformed to rutile nanocrystals upon reaching a particular size greater than 11–17 nm. Then the rutile nanocrystals grow remarkably faster [4, 8]. Zhang, Banfield and colleagues have examined the size dependence of the phase transition from anatase to rutile nanocrystals through thermodynamic [7, 8, 23] and kinetic [7, 19, 24] approaches. In a recent review Hanaor and Sorrell [25] have discussed the anatase to rutile phase transformation focusing mainly on the thermodynamics and the factors (synthesis, dopants) influencing such a transformation.

In the present work we attempt to compare directly phase transition and textural changes taking place upon calcination (thermal treatment) of pure anatase and a mixed titania consisting of anatase and rutile. For this reason we investigate the influence of calcination temperature and time on the structure and texture of two very popular commercial TiO₂ samples, namely a pure anatase purchased from Alfa Aesar and the Degussa P25 consisting of anatase and rutile. Another goal of the present work is the achievement of a severe control of the anatase/rutile ratio, a critical photo-catalytic parameter, by regulating properly the calcination temperature and time. N₂ physisorption was used to determine the textural properties of the parent and calcined samples. Structural changes and their kinetics were monitored using in-situ and ex-situ X-ray powder diffraction (XRD). Thermogravimetric Analysis / Differential Scanning Calorimetry (TGA/DSC) was employed to examine the thermal events of the samples through heat treatment. The effect of sample composition on electronic transitions was studied through Diffuse Reflectance Spectroscopy (UV-vis DRS) in the ultra violet and visible spectrum range.

2. Experimental

Two commercial samples of titania were used. The first (P25) was TiO₂ powder purchased from Degussa and consists of anatase (~80%) and rutile (~20%). The second sample (AA) was pure anatase extrudates (with diameter 3 mm) purchased by Alfa Aesar. These extrudates were crushed by an electrical achate mortar and sieved to obtain powder with particle size lower than 105 μm. The samples were calcined in air at various temperatures and time intervals. The calcined samples were denoted as P25-t-T and AA-t-T, where t and T stand for calcination time in hours and temperature in Celsius degrees, respectively.

The determination of the textural properties, namely, the specific surface area (SSA), the pore volume (PV), and the mean pore diameter of the samples was based on the nitrogen adsorption-desorption isotherms. A static methodology was applied using a Micromeritics apparatus (Tristar 3000 porosimeter) and the corresponding software.

XRD measurements were carried out with a Bruker D8 Advance X-Ray diffractometer equipped with nickel-filtered Cu Ka

(0.15418 nm) radiation source. The step size and the time per step were respectively fixed at 0.02° and 0.5 s in the range of 20° ≤ 2θ ≤ 80°. Two series of XRD patterns were recorded. In the first series the XRD patterns of samples calcined at various temperatures and time intervals have been recorded at room temperature (ex-situ). In the second series XRD patterns of non-calcined samples were recorded upon calcination (in-situ) in a temperature programmed furnace (TP-XRD). The temperature increased stepwise applying 50 °C steps up to 800 °C with a heating rate of 5 °C min⁻¹ under static air. The sample remained in each temperature step for the time needed in order the corresponding XRD pattern to be recorded. The percentage of anatase and rutile in the studied materials was calculated using their most intensive peaks and their sensitivity factors balanced towards corundum (I/I_c method), using the DIFFRAC^{PLUS}EVA (Bruker AXS) evaluation software package. The mean crystallite size was estimated using the Scherrer equation [26].

TGA/DSC measurements were carried out by a STA 449 C (Netzsch-Gerätebau, GmbH, Germany) equipment. The heating range was extended from room temperature up to 1000 °C, with a heating rate of 2 °C min⁻¹ under synthetic air flow rate of 30 cm³ min⁻¹.

The diffuse reflectance spectra of the calcined samples were recorded in the range 200–800 nm at room temperature. A UV-Vis spectrophotometer (Varian Cary 3) equipped with an integration sphere has been used. Polytetrafluoroethylene (PTFE) was used as reference. The samples were mounted in a quartz cell. This provided a sample thickness greater than 3 mm to guarantee the “infinite” sample thickness.

3. Results

3.1. Characterization upon calcination

The crystal structure of the samples calcined at various temperatures was investigated directly using TP-XRD analysis. The corresponding XRD patterns are illustrated in Fig. 1.

Inspection of Fig. 1(a) shows that the P25 sample consists of anatase (main peak: 2θ=25.3°) and rutile (main peak: 2θ=27.5°) polymorphs, in agreement with the Degussa data according to which this material consists of ~80% anatase and ~20% rutile. As the heating temperature increases a gradual transformation of anatase to rutile is observed.

Using the corresponding patterns the percentage composition in anatase of the P25 sample has been calculated at each temperature and presented in Table 1. These values show that the composition of the P25 sample (%A) remains unchanged up to 650 °C under the heating conditions adopted upon TP-XRD analysis. Then, the anatase (rutile) portion decreases (increases) dramatically as the heating temperature increases up to 800 °C. The mean diameters of the anatase and rutile crystals have been calculated at each temperature using the main peaks of the two crystallographic forms. The calculated values are also compiled in Table 1. These values show that the crystal size of both phases increases remarkably with the temperature in the range 650–800 °C.

Investigation of Fig. 1(b) shows that no transformation of anatase to rutile takes place in the AA sample (pure anatase) as the temperature increases up to 800 °C. Careful observation of these TP-XRD patterns shows that the anatase peaks become higher and sharper as the temperature increases. This means that the crystallinity of this material increases as the temperature increases. This is reflected in the mean diameter values of the anatase crystals (d_A) (Table 1).

The different influence of the calcination temperature on

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