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Effect of 2-propanol and water contents on the crystallization and particle size of titanium dioxide synthesized at low-temperature

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Abstract

Two series of titanium dioxide, TiO_2, powder were prepared at a temperature of 50 °C without any catalyst. The effects of 2-propanol and water contents on the formation of crystalline powder mixture of anatase and brookite were systematically studied. The characteristics of produced powder were determined by employing X-ray diffraction, transmission electron microscopy, nitrogen adsorption test and Fourier transform infrared spectroscopy.

The obtained results showed that increases in the amount of water used in the powder synthesis turned the product from amorphous to the crystalline anatase structure with small traces of brookite. The results also clearly showed that the use of 2-propanol in the synthesis hindered the crystallization of TiO_2. Furthermore, the specific surface area of TiO_2 nanopowder decreased and the particle size increased when more water was used in the synthesis. These results are presented and discussed in this paper.

Keywords: A. Powders: chemical preparation; A. Sol–gel processes; D. TiO_2

1. Introduction

Titanium dioxide, TiO_2, has three polymorphs: rutile, anatase and brookite. TiO_2 is extensively used in cosmetics, paints and food products because it is stable, inexpensive and non-toxic as well as has a high index of reflection. Photocatalytic activity of TiO_2 has also been widely reported and discussed in literature due to promising applications of TiO_2 in the production of hydrogen or mineralization of several organic pollutants. In photocatalytic applications, the used phases of TiO_2 are anatase and rutile [1–5].

Numerous methods have been employed for the controlled formation of crystalline TiO_2 coatings and nanoparticles. Promising technique is, for example, a sol–gel method, primarily via the hydrothermal and solvothermal processing routes based on alkoxide (M-OR) or titanium(IV) chloride precursors [6–8]. These techniques offer the effective routes to prepare titanium dioxide with a good control of particle size and phase composition as well as high homogeneity in particle distribution [6–9]. In these syntheses methods, precursors are typically dissolved into organic solvent after which they undergo hydrolysis and condensation reactions with the added water. The reactions and the structure of the final product can be controlled by adjusting process parameters, such as temperature and the amount of catalyst [10–12]. The result of hydrolysis and condensation of titanium-containing alkoxide is the formation of (TiO_6) octahedra. The crystal structure of TiO_2 depends on how these octahedra (TiO_6) are linked to each other. Final structure of anatase and rutile is tetragonal, whereas brookite is orthorhombic [12–14]. One method to obtain desired crystal structure of TiO_2 powder is the heat treatment of amorphous titanium hydroxide [15]. However, crystallization by heat treatment has been reported to increase the particle size and to decrease the specific surface area [12–14]. That is the main reason why the low-temperature synthesis methods like hydrothermal, solvothermal and other modified synthesis methods to prepare crystalline TiO_2 are applied [12,13,16–18].

In this study, two series (denoted as S1 and S2) of TiO_2 powders are synthesized by hydrothermal method under

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ambient pressure at a temperature of 50 °C. The first series (S1) was synthesized in a water-alkoxide-2-propanol mixed solution and the another series (S2) in a solution of only water and alkoxide. These two series were synthesized in order to find out the effects of 2-propanol and water contents on the formation of crystalline titanium dioxide at low temperature; to the best of our knowledge, no earlier studies report the influence of the amount of 2-propanol used in the synthesis on the crystallization of TiO_2. The synthesized powders were then characterized in terms of phase composition, specific surface area, particle size, morphology and surface groups involved.

2. Experimental procedure

2.1. Preparation of TiO_2 powders

The starting precursors were tetra-n-butyl orthotitanate alkoxide (denoted as $C_{16}H_{36}O_4Ti$, purity > 98%, VWR), 2-propanol (denoted as C_3H_7OH, purity > 99.5%, VWR) and ion-exchanged water. All chemicals used in this study were reagent-grade and no further purification was done. Two series of powders were synthesized, denoted as S1 and S2. For the powders S1, 1.875 ml tetra-n-butyl orthotitanate liquid was diluted with 6.25 ml of 2-propanol. The solution was stirred for 15 min before a varying amount of ion-exchanged water was added into it. The powders of the first series were labeled as $S1_1$, $S1_2$, $S1_3$, $S1_4$, $S1_5$ and $S1_6$. For the powders S2, a varying amount of ion-exchanged water was added into tetra-n-butyl orthotitanate. 2-propanol was not used at all in the series S2. The obtained powders were labeled as $S2_1$, $S2_2$, $S2_3$, $S2_4$, $S2_5$ and $S2_6$. The molar ratios of water/2-propanol and water/tetra-n-butyl orthotitanate used in the syntheses are listed in Table 1.

After the ion-exchanged water was added into the solutions, these were further stirred for 24 h at 50 °C under atmospheric pressure. After this period, the precipitated powders were separated by filtering and finally dried in a furnace at 50 °C for 24 h. The experimental procedures for processing TiO_2 nanoparticles are described in Fig. 1.

Table 1
The molar ratio of water/2-propanol and water/tetra-n-butyl orthotitanate for powder syntheses.

Sample	The molar ratio of water/2-propanol	The molar ratio of water/tetra-n-butyl orthotitanate
$S1_1$	1.0	15
$S1_2$	1.7	25
$S1_3$	2.3	35
$S1_4$	3.3	50
$S1_5$	7.3	112
$S1_6$	15	230
$S2_1$	–	15
$S2_2$	–	25
$S2_3$	–	35
$S2_4$	–	50
$S2_5$	–	112
$S2_6$	–	230

2.2. Characterization of the powders

The crystal structure of TiO_2 powders was determined by using a Siemens Kristalloflex D-500 X-ray diffractometer and a monochromatized CuKα radiation over the range of $20° < 2\theta < 70°$. The crystal size were estimated from smoothed XRD-patterns, using a Scherrer formula $t = (0.9\lambda / B\cos\theta)$ [19], where t is the size in nm, λ is the wavelength of X-rays in nm (0.15418 nm), B is the full width half maxima of the peak in radians and θ is the Bragg angle. The specific surface area of the powders was measured by nitrogen adsorption tests using a Brunauer–Emmett–Teller (BET) method and Colter Omnisorp 100 cx device. The average size of the particles was calculated using the following equation: $d_{BET} = 6/(\rho S_{ssa})$, where ρ is the density and S_{ssa} is the specific surface area. The morphology of the particles was determined by using a JEOL JEM 2010 transmission electron microscope (TEM) and the accelerating voltage of 200 kV. Surface groups of the powders were examined using a Perkin Elmer Spectrum One Fourier transform infrared spectrometer (FTIR) in the wavenumber range of 4000–450 cm^{-1}.

3. Results

3.1. Structural analysis

Figs. 2 and 3 show the raw XRD patterns for the powder samples. The pattern in Fig. 2(a) shows the amorphous nature of the $S1_1$ precipitate obtained using the lowest water/2-propanol ratio within series S1. The patterns in Fig. 2(b and c) and related to $S1_2$ and $S1_3$ show that the powders were still mainly amorphous, with minor peaks of crystalline anatase phase being also detected. Clear peaks of crystalline anatase phase and a small trace of brookite (121) at $2\theta = 30.8$ were detected in XRD patterns $S1_4$, $S1_5$ and $S1_6$ in Fig. 2(d–f), respectively. The obtained results indicate that after the molar ratio of water/2-propanol was 3.3 only minor changes in the intensity and width of the diffraction peaks occurred (Fig. 2(d–f)) with the increasing amount of water. Hence, the main finding was that the lowest used amount of water yielded an amorphous precipitate but with increases in the amount of water, the precipitate crystallized to anatase with small traces of brookite.

The XRD spectra of powders synthesized without 2-propanol (series S2) are shown in Fig. 3(a–f). The pattern presented in Fig. 3(a) revealed crystalline nature of the powder synthesized with the lowest amount of water ($S2_1$). Although peaks were clearly detectable, the overall intensity of the pattern in Fig. 3(a) was quite low, meaning that the powder $S2_1$ was poorly crystallized. With increase in the amount of water, peaks became more evident and the intensity of the peaks higher, indicating more complete crystallization. However, when comparing the XRD spectra for powders synthesized with 2-propanol (Fig. 2) to those for powders synthesized without it (Fig. 3), it may be clearly seen that the presence of 2-propanol in the precursor solution inhibited the crystallization of TiO_2. With the same amount of water used in the