



Absolute crystallinity and photocatalytic activity of brookite TiO₂ samples



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ABSTRACT

This study reports a method to determine the absolute crystallinity of partly crystalline brookite TiO₂ photocatalysts. A natural, a commercial and various home-prepared brookite powders were characterized by X-ray diffraction analysis, Raman spectroscopy, scanning electron microscopy, UV–vis diffuse reflectance spectroscopy and nitrogen adsorption measurements. The absolute crystallinity was calculated from the ratio between the full width at half maximum intensity of the (121) X-ray diffraction peaks of the brookite samples and the (111) peak of CaF₂ as internal standard. The photocatalytic activity of the powders was tested employing the photodegradation of 4-nitrophenol as well as the selective oxidation of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde (*p*-anisaldehyde) under UV irradiation. The results indicated that crystallinity positively influenced the photooxidation of 4-nitrophenol and 4-methoxybenzyl alcohol but reduced the selectivity toward the synthesis of *p*-anisaldehyde.

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1. Introduction

Titanium dioxide (TiO₂) is the most studied photocatalyst because of its high efficiency, non-toxicity, chemical and biological stability, and low cost. TiO₂ exists mainly in three different crystalline habits: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Pure brookite is rather difficult to be prepared so that its photocatalytic properties have been not much studied. Anatase is generally accepted to be a photocatalyst more efficient than rutile and brookite but recently, brookite has showed to be an interesting candidate for photocatalytic applications [1–13].

The photocatalytic activity of a TiO₂ powder depends on its physical properties such as crystal structure, degree of crystallinity, surface area, particle size and shape, surface hydroxyls content, etc. Brookite is composed of octahedra, each with a titanium atom at its center and oxygen atoms at its corners. The octahedra share edges and corners with each other to such an extent as to give the crystal the correct chemical composition [14]. Band gap energies ranging from 3.1 to 3.4 eV have been reported for brookite [1]. These values depended on the method of preparation and on the content of amorphous phase present in the samples.

The physical properties of brookite can be changed by calcination at different temperatures [2,5–8]. Thermal treatment increases crystallite size and crystallinity of the pristine sample [3,8,15] and decreases the surface area and the surface hydroxylation degree. Each of these parameters affects in different way the photocatalytic activity [16].

The presence of amorphous phase in TiO₂ samples is commonly considered to have no influence on the photocatalytic activity. This assumption, acceptable when the amount of amorphous phase is low, can be erroneous if its content becomes important. Ohtani et al. [17] showed that amorphous titania exhibits negligible reactivity in several photocatalytic reactions due to the facilitated recombination of electrons and holes at the traps on the surface and in the bulk of the particles. The increase of crystallinity leads to the reduction of crystal defects of the structure improving the separation rate of the photoinduced e⁻/h⁺ pairs.

Crystallite size and crystallinity can be evaluated by X-ray diffraction analysis. Inagaki et al. [18–20] qualitatively estimated the crystallinity of anatase powders by the full width at half maximum (FWHM) intensity of the 101 diffraction line of the X-ray powder patterns. To the best of our knowledge, only few papers have reported a quantitative analysis of the crystallinity of TiO₂ powders [21–25]. Ohtani et al. [17] evaluated the weight fraction of crystalline anatase in amorphous-anatase mixtures by means of differential scanning calorimetry (DSC) and powder X-ray diffraction (XRD) measurements. Jensen et al. [21–23] determined the

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absolute crystallinity of anatase and rutile for different TiO₂ photocatalysts by X-ray diffraction analysis. No determination of the absolute crystallinity of brookite samples has ever been published.

The aim of this work was to determine the absolute crystallinity of brookite TiO₂ powders and to study the correlation between the photocatalytic activity of the samples and several properties, including crystallinity degree, surface area and particle size. The influence of the calcination temperature was also investigated. The samples were characterized by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), and BET specific surface area measurements. The photocatalytic activity was determined using the degradation of 4-nitrophenol (4-NP) and the selective oxidation of 4-methoxybenzyl alcohol (4-MBA) to 4-methoxybenzaldehyde (*p*-anisaldehyde, PAA) under UV light irradiation. The absolute crystallinity of the samples was determined by the XRD patterns using a simple quantitative method that can be used for partly crystalline brookite photocatalysts.

2. Experimental

2.1. Materials and instruments

Natural brookite used in this work was obtained from crystals collected from the Magnet Cove Complex, Arkansas (USA). The Cove is a 100-million-year old intrusive igneous body created by mantle-derived magma that pierced through existing Paleozoic sedimentary rocks. The average composition of the material was: Ti (0.965), Nb (0.017), V (0.008), Fe (0.008), Si (0.001) and Mg (0.001) [26]. The brookite crystals were black, due to interdispersed niobium practically impossible to be physically separated. Commercial brookite (99.99%) was supplied by Sigma as a flocculent white powder. Home-made brookite powder was obtained as follows: 10 mL of TiCl₄ were added dropwise to a solution containing 420 mL of water and 160 mL of concentrated hydrochloric acid at room temperature under stirring. Then the solution was heated in a closed bottle and aged for 48 h in an oven at 100 °C. The resultant precipitate contained a brookite–rutile mixture. Pure brookite was separated by peptization through several cycles of supernatant removal followed by water addition up to the initial volume. After a few washings, a dispersion of brookite particles formed, while the rutile phase remained as precipitate and it could thus be separated [27]. After removing the supernatant liquid, the obtained powders were collected and dried in vacuo at 55 °C. The home-made sample is referred as HP 100 °C.

X-ray diffraction patterns of the powders were recorded at room temperature on a PANalytical Empyrean diffractometer equipped with a PIXcel^{1D} (tm) detector using the CuK α radiation and a 2 θ scan rate of 1.28 min⁻¹. The crystallite size of the samples was calculated by using the Scherrer equation. Raman spectra were obtained by means of a BWTek-i-micro Raman Plus System, equipped with a 785 nm diode laser. The power of the laser was 15% of the maximum value that was about 300 mW. The measurements were performed focusing the sample by a 20 \times magnification lens with a spot size of about 50 mm. The accuracy of the Raman shift was approximately 3 cm⁻¹. Scanning electron microscopy (SEM) observations were obtained using a FEI Quanta 200 ESEM microscope, operating at 20 kV on specimens upon which a thin layer of gold was deposited. An electron microprobe used in an energy dispersive mode (EDX) was employed to obtain information on the actual content of elements present in the samples.

The specific surface areas were determined with a Micromeritics ASAPTM 2020 apparatus by using the five-points BET method. Pore volume and pore area distributions were obtained by the BJH method from the nitrogen adsorption-desorption isotherms

at the liquid nitrogen temperature. Visible-ultraviolet spectra were recorded by diffuse reflectance spectroscopy in the range 200–800 nm by using a Shimadzu UV-2401 PC instrument with BaSO₄ as the reference sample. Photoluminescence (PL) spectra were recorded at room temperature with a Perkin Elmer LS45 Luminescence Spectrometry by exciting the samples at 320 nm.

The point of zero charge (pzc) of the samples was determined by the method of mass titration, which involves finding the asymptotic value of the pH of an oxide/water slurry as the oxide mass content is increased [28]. Thermogravimetric analysis was performed in the 30–750 °C range by means of a Netzsch Simultaneous Thermal Analyzer STA 449 Jupiter F1 with a nitrogen flux of ca. 20 mL min⁻¹, using alumina crucibles. The temperature program consisted of three steps: heating from 30 to 120 °C at 10 °C min⁻¹, isothermal step at 120 °C for 15 min, heating from 120 to 750 °C at 10 °C min⁻¹.

2.2. Photoreactivity experiments

2.2.1. 4-Nitrophenol degradation

A 0.5 L Pyrex batch reactor of cylindrical shape was used. In a typical experiment, 0.6 mg mL⁻¹ of catalyst were suspended in an aqueous solution containing 20 mg L⁻¹ of 4-nitrophenol (4-NP). The light source was a 125 W medium pressure Hg lamp (Helios Italquartz, Italy) with a maximum emission at about 365 nm, axially positioned within the photoreactor. The temperature of the suspension was controlled by circulation of water through a Pyrex thimble surrounding the lamp. The photon flux emitted by the lamp was $\Phi_1 = 11 \text{ mW cm}^{-2}$. O₂ was continuously bubbled for ca. 0.5 h before switching on the lamp and throughout the occurrence of the photoreactivity experiments. The temperature inside the reactor was ca. 30 °C. Samples of 5 mL were withdrawn at fixed intervals of time with a syringe, and the catalyst was separated from the solution by filtration through 0.2 μm Teflon membranes (Whatman). The quantitative determination of 4-nitrophenol was performed by measuring its absorption at 315 nm.

2.2.2. 4-Methoxybenzyl alcohol oxidation

The experiments were carried out in a cylindrical photoreactor (CPR, internal diameter: 32 mm and height: 188 mm) containing 150 mL of a suspension obtained adding 90 mg of catalyst to an aqueous solution of 4-methoxybenzyl alcohol at natural pH. The initial 4-MBA concentration was 0.5 mM. The reactor was irradiated by three external Actinic BL TL MINI 15 W/10 Philips fluorescent lamps whose main emission peak was in the near-UV region at 365 nm. The radiation intensity impinging on the suspension was measured by a radiometer Delta Ohm DO9721 with a UVA probe; the radiation power absorbed per unit volume of the suspension was about 0.76 mW mL⁻¹. The runs were carried out by using atmospheric air as oxidant agent and the lamps were switched on at time $t=0$, after 0.5 h from the starting of the aeration. The temperature inside the reactor was ca. 30 °C. The values of substrate concentration before the addition of catalyst and before starting the irradiation were measured in order to determine the substrate adsorption on the catalyst surface under dark conditions. During the photoreactivity runs samples were withdrawn at fixed times and immediately filtered through 0.2 μm membranes (HA, Millipore) before analyses. The quantitative determination and identification of the starting molecules and their oxidation products were performed by means of a Beckman Coulter HPLC (System Gold 126 Solvent Module and 168 Diode Array Detector), equipped with a Phenomenex Kinetex 5 mm C18 100A column (4.6 mm \times 150 mm) working at room temperature. The eluent consisted of a mixture of acetonitrile and 1 mM trifluoroacetic acid aqueous solution (20:80 volumetric ratio) and the flow rate was 0.8 mL min⁻¹. Retention times and UV spectra of the compounds

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