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Influence of acid precursors on physicochemical properties of nanosized titania synthesized by thermal-hydrolysis method

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Abstract

The influence of nature and concentration of acid species on surface morphology and physicochemical properties of titania particles synthesized by direct thermal hydrolysis of titanium tetrachloride was investigated. The acids used were hydrochloric acid, nitric acid, sulfuric acid, and perchloric acid with a concentration of 3 M. Thermal hydrolysis of titanium tetrachloride in hydrochloric acid and perchloric acid with molar ratios of $[H^+]/[Ti^{4+}]$ = 0.5, 1.0, 1.5, and 2.0, respectively, was used to study the effect of acid concentration. The synthesized materials were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, dynamic light scattering, and thermogravimetric analysis. Characterization of the samples by X-ray diffraction studies revealed the influence of acid species on the phase transformation of titania. Samples prepared by hydrochloric acid, nitric acid, and perchloric acid formed rutile phase with rhombus primary particles, while sulfuric acid resulted in anatase phase with flake-shaped primary particles. Transmission electron microscopy and dynamic light scattering results confirmed the nanosized titania particles and the agglomeration of primary particles to form secondary particles in spherical shape. The particle size of titania prepared using perchloric acid was smaller than those prepared with other acid sources. A direct correlation between $[H^+]/[Ti^{4+}]$ ratio and particle size of titania was observed.

Keywords: A. Oxides; B. Chemical synthesis; C. Electron microscopy; D. Surface properties

1. Introduction

During the past few decades, the scientific and technological interest in the application of semiconductor photocatalyst has grown exponentially. Titania has been widely used [1–4] and its applications include in paints and cosmetics industries, catalysis, and photocatalysis [5]. Titania is also a common material for photovoltaic cells and appears to be interesting as a dielectric material for the next generation of ultra-thin capacitors due to its high dielectric constant [6]. The photocatalytic activity of titania, which is known for approximately 60 years, has been investigated extensively. The discovery of the photocatalytic performance of titania by Fujishima and Honda [1] marked the beginning of a new era in heterogeneous photocatalysis. The uses and performances for a given application are, however, strongly influenced by the crystalline structure, morphology, and the size of the particles [7–10]. Particle size of titania is a vital physical parameter in a catalyst, because it can directly affect the number of active sites. Indeed, as

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many other solids, nanosized titania particles are of particular interest because of their specifically size-related properties. Hence, many works have focused on the synthesis of titania nanoparticles [11,12].

Anatase and rutile are the polymorphs of titania commonly obtained by the hydrolysis of titanium compounds, such as titanium tetrachloride ($TiCl_4$) or titanium alkoxide, in solution [13]. Anatase is thermodynamically metastable up to 800 °C and an anatase–rutile transition occurs above this temperature. The rutile obtained, however, does not change into anatase after cooling due to the high activation energy of the back transition. The two crystal structures differ by the distortion of each octahedron and by the assembly pattern of the octahedra chain. Brookite is observed sometimes as a by-product when the precipitation is carried out in an acidic medium at low temperature. Classically, brookite is obtained as large crystals by hydrothermal methods at high temperature and pressure in aqueous or in organic media.

The advantages of using titania in the photocatalytic decomposition of organic pollutants are based on its remarkable activity, low cost, chemical and radiation stability, and its non-toxic properties. Moreover, no strong oxidizing agents, such as O_3 or H_2O_2, are required for photodecomposition [14]. Many studies have shown the relations between crystallographic structure and surface characteristics and their effects on the catalytic properties [15,16].

In recent years, a number of methods have been reported to prepare titania, such as sol–gel [17,18], chemical vapor deposition, hydrothermal [19], peptization, and microemulsion methods [20]. Recently, the microemulsion method has been successfully applied to synthesize nanosized titania particles with titanium alkoxide as the starting material [21,22]. Since the ratio of aqueous phase to oil phase and surfactant in these microemulsion systems is too small and therefore only a small amount of nanosized titania particles can be obtained at the cost of a large amount of oil and surfactant.

Recently, many different methods have been used in preparing titania nanoparticles. Among these, precipitation of $TiCl_4$ [23,24], $Ti(SO_4)_2$ [25], and sol–gel method [26] have been widely investigated. The sol–gel approach provides a feasible route to prepare nanosized titania particles [27]. However, the aggregation of nanoparticles into larger particles due to high-temperature calcination limits its application that paved way for recent researches, such as supercritical drying, in solving this problem. However, in spite of so many efforts, it is still unclear about the most convenient method in terms of mechanical stability and photocatalytic activity. More attention has been paid to thermal-hydrolysis method owing to its milder reaction conditions [28,29]. Even though numerous studies have been reported about the synthesis of titania particles, there are only few reports [30–32] about the effect of acid species on the properties of titania nanoparticles, which plays a major role in determining the properties of titania.

It is well known that the particle size is one of the factors to influence the photocatalytic performance of titania. In the present work, thermal-hydrolysis method was applied to prepare nanosized titania using $TiCl_4$. The influence of acid species and its concentration on the size and morphology of titania is attempted using various precursors such as HCl, HNO_3, H_2SO_4, and $HClO_4$. The physicochemical properties of the titania prepared will be discussed and correlated with the nature of the acid species.

2. Experimental

2.1. Synthesis of titania

Titania was prepared by thermal hydrolysis of $TiCl_4$ using various acid precursors such as HCl, HNO_3, H_2SO_4, and $HClO_4$. The concentration of $TiCl_4$ and acid species was maintained at 1 and 3 M, respectively. When $TiCl_4$ was dissolved in distilled water, the heat of the exothermic reaction explosively generated the formation of orthotitanic acid, $[Ti(OH)_4]$. HCl, HNO_3, H_2SO_4, and $HClO_4$ were added, respectively, into the aqueous solution of $TiCl_4$. The synthesis was carried out in an oven at 100 °C for 24 h with $[H^+]/[Ti^{4+}]$ ratio of 1 and aging for a period of time. Aqueous NH_4OH was added to adjust the pH value of titania suspension around 4–5 so as to avoid titania particles redissolve in the solution, to remove chloride ion, and to control $[H^+]/[Ti^{4+}] = 1$. The obtained titania was dried in an oven at 100 °C for 24 h.

2.2. Characterization

The crystalline structure of the samples was analyzed by X-ray powder diffraction (XRD) using a Siemens D500 automatic powder diffractometer. Nickel-filtered Cu Kα radiation (λ = 0.15418 nm) was used with a generator voltage