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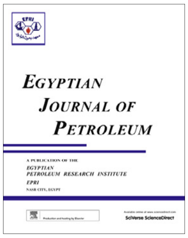

FULL LENGTH ARTICLE

Different outlet for preparing nano-TiO_2 catalysts for the photodegradation of Black B dye in water

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Abstract Two nano-titania catalysts were prepared using two economically varying titanium precursors: titanium tetrachloride (A) and titanium isopropoxide (B). The catalysts were calcined at temperatures of 500 °C, 600 °C and 700 °C and characterized using X-ray diffraction (XRD), electron diffraction (ED), BET surface properties and high resolution transmission microscopy (HRTEM). The calcined catalysts were found to differ markedly in their physical characters and TiO_2 phases produced as well as their photocatalytic activities. The anatase titania phase diminished from 100% to 83% in TiO_2A but from 64% to zero in TiO_2B via temperature increase from 500 °C to 700 °C, due to transforming anatase to rutile. The brookite TiO_2 phase only appeared (17%) in catalyst B500. In general, the catalyst of choice is A600 by virtue of many compositional, economical and catalytic advantages.

1. Introduction

TiO_2 semiconductor in nanoscale is considered as the most promising material for heterogeneous photocatalysis, due to its efficiency for eliminating organic pollutants and industrial residues in aqueous media [1,2]. The advantages of TiO_2 include powerful oxidation strength, high chemical stability, nontoxicity [3,4], photostability [5], high redox potential [6] and ability to produce electron/hole pairs with high life time and low cost [7] makes it a substantial oxide catalyst. Titanium dioxide has three crystalline phases: brookite (orthorhombic), anatase (tetragonal), and rutile (tetragonal). Rutile is the stable phase, whereas anatase and brookite are both metastable at all temperatures [8]. The energy band gaps are equal to 3.2 and 3.0 eV for anatase and rutile phases, respectively, which means that ultraviolet (UV) region of the solar spectrum is the proper region for the photoexcitation of TiO_2 nanoparticles to produce electron/holes and generation of OH radicals [9]. Many studies have indicated that the nanoparticles exhibit special photochemical characteristics [10] compared to the conventional larger particles. Also, the band gap of the nanoparticles increases with the decrease of particle size [11], and other important properties such as morphology, surface area, degree of crystallinity, anatase/rutile ratio which can be controlled during the preparation method and the heat treatment [12]. It has been disclosed that a 70/30% anatase/rutile in Degussa P-25 TiO_2 is conventionally selected as a reference photocatalyst for the oxidation of

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organics [13]. Several methods for TiO_2 nanoparticles preparation have been reported, such as chemical precipitation [14], microemulsion [15], hydrothermal crystallization [16] and sol–gel synthesis [17]. Many workers have studied the changes in morphology of TiO_2 with heat treatment. Porter et al. [18] studied microstructural changes in commercial Degussa P-25 TiO_2 due to heat-treatment. They found that with the increasing of calcination temperature the apparent crystallite size and rutile content in the catalyst increased, whereas the specific surface area and the rate of phenol photodecomposition under UV irradiation decreased. The same effect was observed by Reddy et al. [19]. Inagaki et al. [20] characterized TiO_2 powders obtained by titanium tetraisopropoxide (TTIP) hydrolysis that is annealed in the range from 400 °C to 900 °C for different periods of time. A marked increase in the crystallite size and a decrease in lattice strain were observed for catalysts annealed above 600 °C. The rate of methylene blue degradation in UV increased with increasing calcination temperature of the catalyst from 400 °C to 700 °C. Calcination of the precursors above 700 °C is indicated by a smaller rate constant, mainly due to partial transformation of anatase to rutile [20].

Azo dyes are the largest group of synthetic colorants (60–70%) and are being used in industry for applications such as textiles, papers, leathers, gasoline, additives, foodstuffs, cosmetics, laser materials, xerography, laser printing, etc. Only 45–47% dye stuffs have been reported to be biodegradable due to their insolubility [21]. Because of the toxicity and persistence of azo dyes, their removal from the wastewater has become an important issue of interest during the last few years.

In the present work, TiO_2 nano powder was prepared via two different techniques; sol–gel technique using TTIP as a precursor in acidic medium and precipitation technique using titanium tetrachloride ($TiCl_4$) as a cheaper precursor in basic medium, all at various calcination temperatures, for the purpose of preparing a more impressive nano TiO_2 photodegradative catalyst for organic dye in aqueous medium.

2. Experimental

2.1. Catalyst preparation

Titanium tetrachloride ($TiCl_4$, 15%) was used as a precursor for preparing nanosized TiO_2 powder by *precipitation method* [22] using ammonia solution as precipitating agent and ethanol as dispersing agent. 25 ml $TiCl_4$ was dissolved in 20 ml distilled water in an ice-water bath. The titanium solution was then slowly mixed with 30 ml distilled water and 20 ml ethanol under vigorous stirring, then ammonia solution was added drop-wise until pH = 9. During the ammonic addition, an intensive precipitation occurred. After the solvent was evaporated at 80 °C for 24 h, the precipitates were dried at 300 °C for 2 h to remove NH_4Cl, then calcined in an air stream at 500 °C, 600 °C and 700 °C for 4 h, hence the catalysts were named A500; A600 and A700, respectively.

A second method for TiO_2 nanoparticle preparation "*sol–gel method*" [23] was used where $Ti(OH)_4$ sol was prepared by mixing 5 ml titanium tetraisopropoxide ($Ti(OCH(CH_3)_2)_4$, 99.5%, Aldrich) with 50 ml isopropanol (Adwic, A.R.) under vigorous stirring. The mixture was then allowed to undergo partial hydrolysis at room temperature by drop-wise addition of 5 ml isopropanol and 2 ml hydrochloric acid (pH = 3–4) with constant stirring. $Ti(OH)_4$ gel was dried at 100 °C overnight then calcined in an air stream at 500 °C, 600 °C or 700 °C for 4 h each. These catalysts were named B500, B600 and B700, respectively.

2.2. Photocatalytic degradation procedure

The degradation of azo dye black b was employed in the current study as an indication for the prepared nano TiO_2 solid catalyst activity parameter. The chemical structure of the dye is illustrated herein.

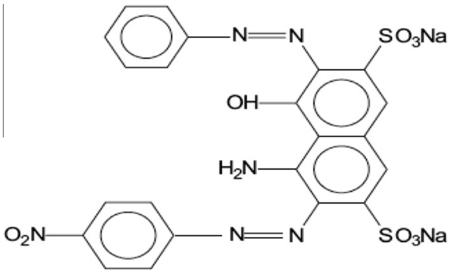
Photodegradation was carried out in air using Pyrex glass made reactor containing 500 ml of the dye solution. The photocatalyst was maintained in suspension by magnetic stirring. In all experiments, air was bubbled continuously through the suspension. The suspension was irradiated with an UV 254 nm (8 W) lamp. All experiments were performed at 25 ± 1 °C. A previously determined optimum concentration of TiO_2 in suspension was 0.5 g L^{-1}, while the dye concentration was 25 ppm in all experiments. The suspension was first stirred in the dark for 30 min to reach the equilibrium adsorption. During both dark adsorption and UV-irradiation periods, samples of 5 ml were collected every hour and filtrated. The discoloration was monitored by measuring the absorbance at λ_{max} = 615 nm, using JENWAY-6505 UV–visible spectrophotometer. Each experiment was carried out for 5 h. Moreover, the pseudo-first-order rate constant (k, h^{-1}) for the photocatalytic degradation of black-b was determined by Eq. (1) [24]:

$$\ln\frac{C}{C_0} = kt \qquad (1)$$

The k value was calculated from a plot of $\ln(C_0/C)$ *vs.* irradiation time (t), where C_0 and C denote the black-b concentrations at t = 0 and t = t, respectively. The pseudo-first-order rate constant was used as an indicator for evaluating the photocatalytic activity of the synthesized TiO_2 photocatalysts.

2.3. Physical characterization of the catalysts

The specific area of all nano TiO_2 catalysts was measured using the BET technique under N_2 gas to validate surface area and texture characterization changes with the preparation conditions. Surface area, pore volume and pore size distribution were evaluated using NOVA2000 gas sorption analyzer (Quantachrome Corporation) system. For each measurement,



Scheme 1 Chemical structure of Amido black 10 b dye.