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Enhanced photocatalytic activity of single-phase, nanocomposite and physically mixed TiO_2 polymorphs

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ABSTRACT

In this study, testing of TiO_2 polymorphs (anatase, rutile, brookite) and their mixtures (anatase/rutile, anatase/TiO_2-B) in heterogeneous photocatalytic oxidation process was conducted at ambient conditions in a batch slurry reactor. The efficiency of bare TiO_2 catalysts was evaluated based on the degree of bisphenol A (BPA) removal, which is a well-known endocrine disrupting compound (EDC). The obtained results indisputably show that BPA removal is strongly affected by catalyst morphology, crystallite size, structure and specific surface area. Detailed interpretation of catalyst properties combined with BPA removal rates leads to the conclusion that photocatalytic oxidation is the most prominent either by using pure anatase particles or high surface area anatase/TiO_2-B nanocomposite. However, the highest extent of mineralization was observed in the presence of high specific surface area nanotubular anatase/TiO_2-B nanocomposite. Interestingly, when anatase and rutile particles were physically mixed, an additional beneficial effect on BPA degradation was observed. Interpretation of the obtained results shows that a synergistic effect between the respective phases takes place, and consequently enhances the overall activity. This phenomenon was explained by the proposed mechanism of overall hydroxyl radicals concentration increment due to transfer of $OH^{\bullet}$ formed on the surface of anatase particles (via H_2O oxidation with photogenerated holes in the valence band) to rutile particles.

1. Introduction

Titanium dioxide (TiO_2) has been used as a white pigment from ancient times, and consequently, it is safety to humans and the environment is guaranteed by history [1]. It can mainly be found in three different crystalline forms: anatase, rutile and brookite. Anatase adopts a tetragonal structure in which four edges are shared per octahedron, but there is no corner sharing. Similarly, rutile also has a tetragonal structure in which two opposite edges of octahedron are shared in order to form a linear chain along [0 0 1] direction. Further, chains are joined through corner connections. On the other hand, brookite has an orthorhombic structure where octahedron share three edges and also corners [2]. Rutile is the stable form, while anatase and brookite are metastable and can be transformed to rutile when heated. In recent years TiO_2-B has also attracted attention, due to its exclusive relatively opened structure. It is formed when layered hydrogen titanates are subjected to heating [3]. All crystallographic forms of nanocrystalline TiO_2 are of great importance in the view point of applications, since they are applicable in a wide variety of fields, such as optics, cosmetics and solar cells [4]. Anatase can be synthesized by various methods such as sol–gel and hydrothermal synthesis [5,6], while rutile can be prepared via phase transition from anatase using either calcination at temperatures over 600 °C [7] or hydrothermal synthesis [8]. There have been many studies on their performance in photocatalytic processes [9,10]. On the other hand, there have only been a few reports on the synthesis of brookite-type TiO_2. The difficulty in preparing pure brookite TiO_2 samples is probably the reason for the small number of studies on its photocatalytic performance [11]. It is well established that anatase is the most photocatalytically active TiO_2 polymorph, compared to rutile and brookite. The high activity can be contributed to prolonged lifetimes of charge carriers and spatial charge separation [12]. Since efficiency of photocatalysis is largely limited by detrimental electron–hole recombination, coupling of two polymorphs of TiO_2 has proved to be an efficient approach for enhancing electron–hole separation and inhibiting electron–hole recombination. Especially anatase/rutile nanostructure proved to be very efficient, since coupling of anatase and rutile allows the transport of excited electrons from anatase to rutile with lower band energy, and therefore charge recombination can be suppressed [2]. Beside this, there have been some reports on the synergistic effect between physically mixed anatase and rutile

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powders, where higher activity was observed compared to singular phases [13]. Activity of TiO_2 in catalytic applications is, besides crystal form, also influenced by various parameters like crystallinity, impurities, surface area and density of surface hydroxyl groups [14]. It has been widely applied in advanced oxidation processes (AOPs), since they have the capability of exploiting the high reactivity of in situ produced hydroxyl radicals in order to achieve complete abatement and thorough mineralization of different organic pollutants [15–18]. There are many AOPs, such as wet air oxidation (WAO), catalytic wet air oxidation (CWAO), photocatalytic oxidation, foto-Fenton process and ozonation [19]. Among them, heterogeneous photocatalytic oxidation process can be used for oxidation of a wide variety of organics [20]. It makes use of a semiconductor metal oxide as a catalyst and of oxygen as oxidizing agent. TiO_2 is the most widely utilized photocatalyst due to its highly distinctive properties; water insolubility, cost effectiveness, durability and resistance to abrasion [21,22]. TiO_2 as a semiconductor has the ability to activate organic pollutants by hydrogen radical abstraction by valence-band holes, as well as oxygen by conduction-band electrons, because it can easily derogate from the stoichiometric composition, which results in an oxygen deficient surface [23]. High surface area of a catalyst is advantageous, since the number of surface vacant sites for oxygen activation is directly connected to the specific surface area of materials [23].

In the following contribution, the preparation of TiO_2 polymorphs and their influence on the degradation process of water dissolved toxic aromatic compound bisphenol A (BPA), an endocrine disrupting compound [24], is systematically investigated. BPA is known to interfere with normal hormone functions and therefore poses a threat to aquatic life and humans as well [25]. According to Yamamoto et al. [26], it was detected in seven out of ten investigated landfill leachates in concentrations ranging from non-detectable to 17.2 mg/l, thus making it an appropriate candidate as a testing molecule in AOPs. The influence of physical mixtures of anatase and rutile on BPA removal was addressed and explained via a proposed mechanism. To the best of our knowledge, there have yet been no reports made on the influence of TiO_2 polymorphs and their mixtures (coexisting nanocomposites and physical mixtures) on the removal of EDCs. Especially, physical mixtures of TiO_2 polymorphs seem to be a grey area in understanding of the enhanced activity of mixed TiO_2 phases. Photocatalytic experiments were conducted in a batch slurry reactor. Catalyst efficiency was determined by withdrawing liquid-phase samples at pre-selected time intervals, and determining the remaining BPA and total organic carbon (TOC) content by using high-performance liquid chromatography (HPLC) and TOC analyses, respectively. Morphological and textural properties of tested catalysts were examined using SEM, XRD, TPD, UV–vis-DR and BET analytical techniques. CHNS analyses of fresh and spent catalysts were also applied in order to evaluate the amount of carbonaceous deposits on catalyst surface during the reaction, which enabled us to estimate the suitability of prepared catalysts for a long-term purification of BPA in the process of photocatalytic oxidation.

2. Experimental

2.1. Catalyst preparation

Pure anatase (A) phase was prepared by using 0.5 g of titanate nanotubes with BET surface area of 400 m^2/g as a precursor (the preparation procedure is available elsewhere [27]). TiO_2 nanotubes with a layered structure were dispersed in 75 ml of 0.001 M H_3PO_4 solution by means of ultrasonic homogenizer. Afterwards, the mixture was hydrothermally treated in a Teflon-lined autoclave for 24 h at 180 °C. The white pasty material was thoroughly washed with distilled water and dried in vacuum under cryogenic conditions for 24 h.

Pure rutile (R) phase was prepared using room temperature synthesis route, similar to that proposed by Zhang et al. [28], where a certain amount of TTIP (Sigma–Aldrich, ≥97.0%) was dropwise added to 37 ml of 2-propanol (Sigma–Aldrich, p.a., ≥99.8%) under vigorous stirring. Afterwards the obtained solution was subjected to mixing in the presence of an ice bath, while dropwise adding 100 ml of 1 M HCl to form a misty mixture. Stirring in an ice bath was carried on for the next 4 h. The employed procedure has led to the formation of a transparent liquid which was left standing for 21 days at room temperature. White precipitates, which formed during this time period, were collected by means of centrifugation and thoroughly washed with distilled water and dried under cryogenic conditions for 24 h. After drying the material was annealed at 450 °C.

Pure brookite (B) phase was prepared using synthesis route similar to that reported by Nguyen-Phan et al. [29]. TTIP (Sigma–Aldrich, ≥97.0%) was dropwise added to 50 ml of 2-propanol (Sigma–Aldrich, p.a., ≥99.8%) while mixing. Afterwards, 200 ml of 0.1 M NaOH was added and left under vigorous stirring for 2 h. The mixture was later hydrothermally treated in a Teflon-lined autoclave for 72 h at 200 °C. The white pasty material obtained was thoroughly washed with distilled water and dried at 60 °C in an oven for 18 h.

Anatase/rutile (AR) nanocomposite was synthesized using ultrasound assisted sol–gel technique, similar to that reported by Prasad et al. [30]. First, a certain amount of titanium (IV) isopropoxide (Sigma–Aldrich, ≥97.0%) (TTIP) was dropwise added to 50 ml of 2-propanol (Sigma–Aldrich, p.a., ≥99.8%) under vigorous stirring. The formed mixture has been subjected to sonication using ultrasonic bath in order to ensure optimal distribution of TTIP in 2-propanol. Subsequently, urea (Kemika) was added in molar ratio of TiO_2:urea = 1.1:1 in order to induce the formation of crystal lattice defects [31]. After the addition of urea, the mixture was again subjected to sonication in order to achieve optimal mixing of all the present compounds. The obtained sol was converted into gel by dropwise addition of distilled water under forceful mixing. After the hydrolysis, stepwise preparation procedure was continued with sonication in order to achieve formation of localized hot spots by collapse of bubbles due to cavitation [32]. The prepared sample was dried at 60 °C in an oven for 18 h. After drying the obtained material was annealed at 700 °C for 3 h.

For the preparation of anatase/TiO_2-B (ATB) nanocomposite, the material obtained in anatase/rutile preparation process (without the annealing step) was used as a precursor for hydrothermal synthesis of high surface area material with homogeneous morphology. The powder was dispersed in 10 M NaOH using ultrasonic homogenizer and later sealed in a Teflon-lined autoclave, which was filled up to 70% of its volume. The synthesis took place at 130 °C for 12 h. The resulting white material was filtered and thoroughly washed (i) with distilled water and (ii) 0.1 M HCl in order to promote proton exchange mechanism. To preserve the structure, the material was dried in vacuum under cryogenic conditions for 48 h. After drying the material was annealed at 400 °C with the aim of inducing changes in the crystal structure, morphology, surface properties and crystallite size, which could further influence catalytic properties during photocatalytic oxidation of the model pollutant BPA.

2.2. Catalyst characterization

The prepared materials were characterized by means of scanning electron microscopy (Carl Zeiss, model FE-SEM SUPRA 35VP). X-ray powder diffraction patterns were acquired using PANalytical X'pert PRO MPD diffractometer with Cu Kα1 radiation (1.54056 Å)