



Catalytic wet air oxidation of bisphenol A aqueous solution in trickle-bed reactor over single TiO₂ polymorphs and their mixtures

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ABSTRACT

In this study, two series of TiO₂ polymorphs (anatase (A and A1), rutile (R and R1), brookite (B and B1)) and nanocomposite mixtures of TiO₂ polymorphs (anatase A/rutile R (AR), anatase A/TiO₂-B polymorph (ATB), anatase A1/rutile R1/brookite B1 (ARB)) were synthesized and tested in the process of catalytic wet air oxidation (CWAO). The goal was total removal of the endocrine-disrupting chemical bisphenol A and its intermediates from a model aqueous solution. TiO₂ polymorphs A1, B1 and R1 were prepared with a similar synthesis procedure and from the same TiO₂ precursor to investigate the influence of catalyst preparation on their performance. To discover which is the main driving property of the catalyst that enables enhanced BPA degradation and mineralization in the CWAO process, different surface, textural and morphological characterization techniques (XRD, SEM, UV-vis-DRS, FT-IR, TG and N₂ sorption) were used. CHNS elemental analysis was applied to reveal which of catalysts is suitable for use in a long-term CWAO process.

Characterization and catalytic tests of solids examined show that the key factor enabling enhanced activity in the CWAO process is high BET specific surface area of the catalysts. It was found that low specific surface area of a solid can be compensated either by the presence of an appropriate crystallinity, or improved charge separation. Catalysts A, A1 and ATB showed encouraging results of BPA degradation and mineralization in the CWAO process and would also be appropriate for long-term use, since negligibly small amounts of carbonaceous deposits were accumulated on the surface of these solids during tests performed in the period of 40 h.

1. Introduction

Exposure of humans to the endocrine-disrupting chemical bisphenol A (BPA) has been associated with chronic diseases, such as cardiovascular disease, diabetes and serum markers of liver disease [1]. An important source of human exposure to BPA is the consumption of food and drinks that have been in contact with packaging made out of epoxy resins or polycarbonate plastics [2–8] produced from BPA. Contamination of the aquatic environment with BPA mainly occurs from landfill leachates, where BPA is leached from disposed packaging [9].

A commonly used method for the removal of organic pollutants from wastewaters is biological treatment with active sludge, where the pollutant caught in the sludge can cause secondary contamination of the environment [10]. Advance oxidation processes (AOPs) are an effective alternative in purifying non-biodegradable, toxic and estrogenically active organic pollutants from wastewater. AOPs are divided into different processes such as wet air oxidation (WAO), catalytic wet air oxidation (CWAO), photocatalytic oxidation, the photo-Fenton process and (catalytic) ozonation [11–13]. The high reactivity of

hydroxyl radicals in the AOPs is used to achieve complete destruction and mineralization of organic pollutants [14,15].

Application of the WAO process is very attractive for cleaning wastewaters that are too toxic to be treated with biological technology or too dilute for incineration [16], although the use is limited by severe operating conditions and high costs. The addition of the appropriate catalysts into WAO mitigates the operating conditions, enhances the reaction rate, shortens the reaction time and reduces the operating costs [17,18]. In the CWAO process organic pollutants are oxidized by activated O₂ species in the presence of solid catalysts at temperatures between 130 and 250 °C and pressures of 10–50 bar into biodegradable intermediate products, or mineralized to CO₂, water and associated inorganic salts [19]. Metal oxides, mixed metal oxide systems, cerium-based composite oxides and supported (e.g. titanium oxide (TiO₂) [20,21]) noble metal catalysts have been studied in CWAO of various organic pollutants [19]. Only a few studies reported the use of bare TiO₂ as a catalyst in the CWAO process. Pintar et al. [22] used TiO₂ support for Ru and achieved 40% TOC conversion of phenol from an aqueous solution at 240 °C when bare TiO₂ was used. Erjavec et al. [23]

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achieved complete removal of BPA and 70% TOC conversion at 210 °C when using TiO₂ nanotubes annealed at 600 °C. With prolonging the time of CWAO runs, more effective oxidation of organic compounds and reaction intermediates can be achieved [24]. Kaplan et al. [25] recycled the liquid phase (5- to 10-fold recycle) in CWAO over TiO₂ nanotubes, which enabled complete BPA conversion and up to 98% TOC conversion at 200 °C.

Studies [26,27] have shown that in heterogeneous photocatalytic oxidation processes different TiO₂ polymorphs and combinations of various TiO₂ polymorphs exhibit different rates of BPA degradation and mineralization when compared to pure TiO₂ polymorphs. As far as we know, no studies have been carried out in which an influence of different TiO₂ polymorphs or nanocomposites of TiO₂ polymorphs, on the degradation of organic pollutants in the CWAO process was examined. Correspondingly, TiO₂ polymorphs (anatase (A and A1), rutile (R and R1), brookite (B and B1)) and nanocomposite mixtures of TiO₂ polymorphs (anatase A/rutile R (AR), anatase A/TiO₂-B polymorph (ATB), anatase A1/rutile R1/brookite B1 (ARB)) were synthesized in the present study and used in the CWAO process to decompose BPA in a model aqueous solution. A series of TiO₂ polymorphs was prepared with a similar synthesis procedure and same TiO₂ precursor so that the influence of these factors on the properties and performance of solids in the CWAO process could be discarded. The CWAO process was carried out in a continuous-flow trickle-bed reactor to investigate the possibility of long-term catalyst use as well as efficient mineralization of BPA and its intermediates. Various characterization techniques were used to determine surface, textural and morphological properties of catalysts before and after the use in CWAO process. To investigate whether the catalysts could be used for long-term mineralization of water dissolved BPA, CHNS elemental analysis of the catalysts was carried out to quantify the accumulation of carbonaceous deposits on the catalyst surface during the CWAO process.

2. Experimental

2.1. Catalyst preparation

Hydrothermal procedure described in detail in our previous work [23] was used to prepare TiO₂ nanotubes, which were used as a precursor to synthesize anatase (A) TiO₂. The obtained TiO₂ nanotubes were dispersed in H₃PO₄ and further hydrothermally treated in a Teflon-lined autoclave. Rutile (R) TiO₂ was prepared using a low-temperature synthesis route proposed by Zhang et al. [28], in which titanium isopropoxide (TTIP, Sigma-Aldrich, ≥97.0%) was used as starting material. Pure brookite (B) was prepared by the synthesis route reported by Nguyen-Phan et al. [29]. Ultrasound assisted sol-gel technique reported by Prasad et al. [30] was used to prepare the anatase/rutile (AR) nanocomposite.

The material obtained in the anatase/rutile preparation process, without annealing, was used as a precursor (P) for the hydrothermal preparation of anatase/TiO₂-B (ATB) nanocomposite.

Detailed synthesis routes for the materials A, R, B, AR and ATB are described in our previous work [26].

To investigate the behaviour of different TiO₂ polymorphs in the CWAO process, we prepared them by utilizing the same starting TiO₂ precursor and synthesis procedure. We used the same material as the precursor for the ATB nanocomposite, and hydrothermal synthesis route under different pH values of solutions. For anatase (A1) synthesis, H₃PO₄ (Merck, 85.0%) was added to the precursor (P), rutile (R1) was prepared in the presence of HCl (Merck, 37.0%) and NaOH (Merck, ≥99.0%) was used to prepare brookite (B1). Finally, we also prepared anatase/rutile/brookite (ARB) nanocomposite for which the precursor (P) was added to HCl (Merck, 37.0%), but the conditions of the hydrothermal procedure were different as in case of R1. More details of the synthesis routes for the materials A1, R1, B1 and ARB are described in our previous work [27].

2.2. Catalyst characterization

X-ray powder diffraction (XRD) patterns of the catalysts were collected on a PANalytical X'pert PRO MPD diffractometer with Cu Kα1 radiation (1.54056 Å) in reflection geometry in the range of 20–90° (steps of 0.034°). Crystalline phases were identified with the use of PDF standards from the International Centre for Diffraction Data (ICDD).

FE-SEM SUPRA 35VP (Carl Zeiss) field-emission scanning electron microscope was used to examine the surface morphology of the synthesized catalysts.

BET specific surface area, total pore volume and average pore size were determined using N₂ sorption isotherms at –196 °C (Micromeritics, model TriStar II 3020). The samples were degassed before measurements using a SmartPrep degasser (Micromeritics) in a N₂ stream (Linde, purity 6.0) at elevated temperatures (60 min at 90 °C, followed by 240 min at 180 °C). Brunauer, Emmett and Teller (BET) theory was applied in order to calculate the specific surface area of catalysts.

A TG instrument (Perkin Elmer, model Pyris 1) was used to measure the acidic properties of each prepared material. The materials were heated at 180 °C for 120 min in a N₂ flow and then cooled down to room temperature. The surface of the solids was saturated with *n*-propylamine for 10 min. To eliminate the excess of *n*-propylamine from the surface, the materials were purged with N₂ for 60 min. After that the temperature programmed desorption (TPD) of *n*-propylamine was conducted by heating to 750 °C at 10 °C/min.

Diffuse reflectance UV–vis spectra of prepared A, R, B, AR and ATB samples in O₂ and N₂ atmospheres at different temperatures (50–250 °C) were recorded using a Perkin Elmer Lambda 650 UV–vis spectrophotometer, equipped with a Praying Mantis accessory (Harrick) to perform measurements in a controlled atmosphere and prescribed temperatures. The scan speed was 120 nm/min and the slit was set to 4 nm. Spectralon[®] was used for background correction.

FT-IR spectra of spent A1, R1, B1 and ARB samples were recorded using a Perkin Elmer Frontier 100 analyzer, equipped with a GladiATR Vision™ (PIKE Technologies) accessory that contained a diamond crystal.

Elemental analysis of fresh and spent catalysts performed with a CHNS analyzer (Perkin Elmer, model 2400 Series II), was employed to evaluate the amount of carbonaceous deposits accumulated on the catalyst surface during CWAO experiments.

To determine the nature of carbon-containing species accumulated on the surface of A1, R1, B1 and ARB solids after use in CWAO runs, TG measurements were performed (Perkin Elmer, model Pyris 1). The samples were heated from 50 to 750 °C in air with a 10 °C/min heating rate.

2.3. BPA oxidation runs in a trickle-bed reactor

CWAO experiments were conducted in a Microactivity-Reference unit (PID Eng&Tech, Spain). It is a computer controlled and fully automated reactor system, which can be defined as a continuous-flow, three-phase trickle-bed reactor with the concurrent down-flow of gas and liquid phase (Fig. 1).

The tubular reactor (Autoclave Engineers, USA), where oxidation of the water-dissolved pollutant occurred, was made of 305 mm (length) × 9 mm (i.d.) Hastelloy C-276 tube and positioned in the central part of the reactor unit. An aqueous solution of BPA (10 mg/l, min. 99%, Sigma-Aldrich) was pumped to the reactor unit by means of a HPLC positive alternative displacement pump (Gilson, model 307). Pure O₂ (Messer, purity 5.0) was fed into the system with the use of a HI-TEC mass-flow controller (Bronkhorst, model EL-FLOW). The pre-heated gas and liquid streams were merged in a T-joint, after that they passed to the reactor tube. A 10 μm sintered stainless-steel (316) filter was located at the top of the reactor to protect the reactor unit from contamination with impurities. The same filter was located also at the

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