

Nanocrystalline TiO₂ polymorphs as catalysts for removal of EDCs using advanced oxidation processes

Renata Kaplan*, Boštjan Erjavec, Albin Pintar

Laboratory for Environmental Sciences and Engineering, National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia

*corresponding author: renata.kaplan@ki.si

Introduction

Titanium dioxide (TiO₂) is the most widely utilized photocatalyst with highly distinctive properties (water insolubility, cost effectiveness, durability and resistance to abrasion). Because it can easily derogate from the stoichiometric composition, which results in an oxygen deficient surface, TiO₂ as a semiconductor has the ability to decompose organic compounds by oxidation by hydroxyl radicals and oxygen radicals formed between adsorbed oxygen and conduction-band electrons [1]. The influence of different physicochemical properties of TiO₂ polymorphs on the removal of bisphenol A (BPA), classified as endocrine disrupting compound (EDC), was thoroughly examined in catalytic wet air oxidation (CWAO) and photocatalytic processes. In this study, a pioneering testing of pure TiO₂ catalysts in CWAO oxidative reaction was performed in a continuous-flow trickle-bed reactor, while the photocatalytic runs were conducted in a slurry batch reactor.

Materials and Methods

Anatase was prepared from titanium (IV) isopropoxide (TIP) using ultrasound assisted sol-gel procedure with subsequent annealing at 500 °C. Rutile was prepared using TIP and isopropanol (IP) mixture dispersed in HCl solution, while mixing in ice bath and left standing for 21 days. Brookite was synthesized by mixing TIP and IP with NaOH solution and subsequent hydrothermal treatment in a Teflon-lined autoclave for 72 h at 200 °C. White precipitates obtained after each synthesis were thoroughly washed with distilled water and dried under cryogenic conditions. The sol-gel technique with subsequent hydrothermal treatment using TIP as a precursor was employed in order to prepare anatase/rutile/TiO₂-B mixture. Anatase/rutile mixture was prepared from TIP utilizing ultrasound assisted sol-gel procedure with subsequent annealing at 700 °C. The obtained materials were characterized by means of TEM, SEM, XRD and N₂ physisorption, etc.

Results and Discussion

Anatase powder with large (100 nm) uniform nanocrystallites (Fig. 1a) showed BET surface area of 28 m²/g. Low temperature synthesis of rutile phase (Fig. 1b) led to monodisperse nanoparticles with BET surface area of 99 m²/g, approximately 100 nm in length and 30 nm in width. After annealing at 450 °C in air atmosphere for 3 h, BET surface area dropped to 32 m²/g. On the other hand, brookite (Fig. 1c) particles showed very low BET surface area (8 m²/g) and interesting humming-top like geometry. Titanate nanotubes, annealed at 400 °C, showed BET surface area of 208 m²/g (Fig. 1d); accordingly to XRD measurements, they consist of anatase (84 %), rutile (11 %) and TiO₂-B (5 %) phases. Hydrothermal synthesis led to the formation of highly uniform particles without undesired secondary particles due to agglomeration. Anatase/rutile (97:3 %) mixture shown in Fig. 1e is highly crystalline material with BET surface area of 9 m²/g. When comparing the results of photocatalytic oxidation of aqueous BPA (Fig. 2a; c(BPA)₀=10 mg/L) we can see that the highly crystalline mixture of

anatase and rutile shows higher activity for the removal of BPA (94 % conversion at t=60 min) than pure anatase phase (69 % conversion).

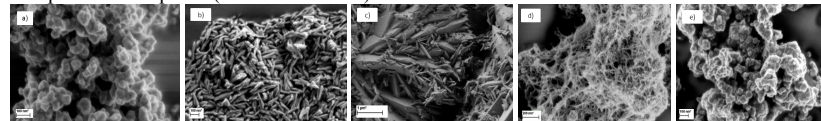


Figure 1: SEM micrographs of a) anatase, b) rutile, c) brookite d) anatase/rutile/TiO₂-B mixture and e) anatase/rutile mixture.

This proves that better charge separation was attained over the solid containing both polymorphs. The presence of additional TiO₂-B phase was not beneficial in this regard. The anatase phase exhibits significantly higher activity for photocatalytic oxidation of BPA, comparing to rutile and brookite. These findings indisputably indicate that BPA conversion is affected by morphology, crystallite size and surface area of the individual catalysts. Due to low concentration of BPA present in the reaction suspension, simplified (L-H) model of pseudo first-order reaction was applied in order to describe the kinetics of BPA disappearance. The obtained apparent first-order reaction rate constants and the corresponding half-lives are presented in Fig. 2b. Regarding CWAO process we can see that high surface area of anatase/rutile/TiO₂-B was beneficial (80 % BPA conversion was monitored in the period of 40 h on stream); however, the contribution of TiO₂-B phase to the overall catalytic activity is not clear yet. Interestingly, anatase/rutile particles enabled 65 % BPA conversion, despite very low surface area, while pure anatase phase exhibited lower performance (50 % conversion) despite three-fold higher surface area. In the case where the catalytic layer in CWAO process consists of physical mixture of two different polymorphs ($m_{\text{anatase}}:m_{\text{brookite}}=1:1$) the conversion is higher (i.e. 60 %), than with the use of singular respective phases (brookite: 45 %, anatase: 50 %).

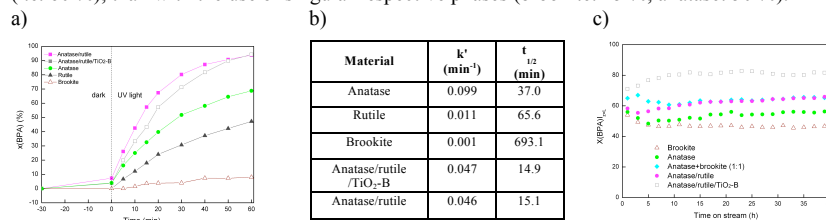


Figure 2: a) BPA conversion as a function of time using different TiO₂ polymorphs in photocatalytic oxidation process; b) first-order reaction rate constants of different TiO₂ polymorphs and corresponding half-lives; c) BPA conversion vs. time on stream using different TiO₂ polymorphs in CWAO process.

Significance

Solely undoped titania polymorphs were used to promote BPA oxidation. Per unit of surface area, highly crystalline anatase/rutile mixture shows the highest potential for the removal of BPA from aqueous solution, regardless the utilized advanced oxidation process.

References

1. Pintar, A.; Besson, M.; Gallezot, P. Applied Catalysis B: Environmental 2001, 30, 123