

Effects of surface fluorination of TiO₂ on the photocatalytic degradation of tetramethylammonium

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Journal of Photochemistry and Photobiology A: Chemistry

Vol. 160, Issue.1-2, 2003

Abstract: Photocatalytic degradation (PCD) of tetramethylammonium (TMA, (CH₃)₄N⁺) ions in water was studied using both naked-TiO₂ and fluorinated-TiO₂ (F-TiO₂) in order to investigate how the modification in TiO₂ surface functional groups affects the PCD reaction. A comparison between the naked-TiO₂ and F-TiO₂ systems shows that their relative photoreactivities strongly depend on pH. At pH 3, the addition of fluoride decreases the PCD rate whereas higher degradation rates are obtained at pH 5 and 7 with F-TiO₂. Little fluoride effect on the TMA degradation rate is observed at pH 9. The addition of fluoride affects not only the PCD rate but also the mechanistic pathways of TMA degradation and subsequently the intermediates and product distribution. The modeling result of TiO₂ surface speciation shows that the fluoride addition at pH 3 shifts the dominant surface species from Ti-OH₂⁺ and Ti-OH to Ti-F (to near completion). This reduces the surface positive charge of TiO₂ (at pH 3) upon adding fluoride and consequently lowers the electrostatic repulsion between the TMA cations and TiO₂ surface. Accordingly, ATR-FTIR spectroscopic measurements show that the TMA concentration at the water/TiO₂ interface is higher on F-TiO₂ than naked-TiO₂ film at pH 3. However, the PCD of TMA on F-TiO₂ at pH 3 is reduced on the contrary, which is ascribed to the depletion of surface OH groups that are the site of surface OH radical formation. At pH 5 and 7, the surface OH sites are not completely diminished even in the presence of fluoride and the presence of surface Ti-F species in fact increases the TMA degradation rate. The fluoride-induced enhancement of PCD is yet to be understood although some speculative arguments are presented. © 2003 Elsevier Science B.V. All rights reserved.