

Chlorine-Doped Visible Light Driven TiO₂ Photocatalysts: Property Changes due to Preparation Condition.

S. K. Joung, T. Amemiya, M. Murabayashi, and K. Itoh

Graduate School of Environment and Information

Sciences,

Yokohama National University, Japan

79-7 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501,

Japan

Introduction

Recently, extensive efforts have been made in the development of visible light driven photocatalysts (PC) that can efficiently utilize solar or indoor light [1]. As results of these efforts, several types of visible light driven PC were recently developed. For instance, the nitrogen-doped TiO₂ reported by Sato [2] and Asahi et al. [3] can be easily prepared, and hence, has been attracting broad interests. However, the nitrogen-doped TiO₂ has a drawback; it is very vivid yellow absorb a large amount of visible light, and its photocatalytic activity depends on absorbance.

We introduce here a new type of visible light driven PC, i.e. chlorine-doped TiO₂ (TiO_{2-x}Cl_{2x}), prepared by evapo-rating sol synthesized from commercial Titanium (III) chloride solution. In this meeting, we introduce the char-acteristic change for preparation condition of the Chlo-rine-doped visible light driven TiO₂ PC.

Experimental

Cl-doped TiO₂ powders were prepared by evaporating sol synthesized from commercial Titanium (III) chloride solution, dehydrated ethanol, and 2N HCl (1:2.2:0.21 mol ratio). The sol was evaporated at different temperatures below 100°C. The powders obtained from sol were pre-treated at different temperatures before use. As a reference, the N-doped TiO₂ (TiO_{2-x}N_x) powders were also prepared by exposing the powders to NH₃ gas at 600°C for 10min. In addition, a UV photocatalyst (ST01, Ishihara Sangyo Kaisha) was used as a reference. The crystalline forms and crystallite sizes of the samples were determined by the X-ray diffraction (XRD) method. X-ray photoelectron spectroscopic (XPS) analysis also can confirm presence of doped chlorine. The visible light absorption of the samples was measured with UV-Visible diffuse reflectance spectra. The photocatalytic activity was evaluated by the change in the concentration of trichloroethylene (TCE), which was monitored by FT-IR. The FT-IR cell used in the experiment was a cylindrical Pyrex-glass batchwise reactor equipped with BaF₂ disks (IR windows) at both ends. The reaction cell was illuminated from upside with visible light (Toshiba Lighting & Technology Co., HQI-TS (250 W), and Fujifilm optical filter SC42 ($\lambda > 420$ nm)).

Conclusion and outlook

XRD patterns of TiO_{2-x}Cl_{2x} powders and the references are shown in Fig. 1. TiO_{2-x}Cl_{2x} powders consisted of mainly anatase, and small amounts of rutile and brookite. The reference TiO₂ powders including nitrogen-doped TiO₂ did not contain brookite and rutile. Brookite was increased the integral intensity for preparation temperature, whereas rutile was decreased. The brookite was observed to disappear with long heating at 500°C or 600°C. We observed presence of Cl (2p_{3/2}) with XPS, whereas the references both TiO_{2-x}N_x and UV photocatalyst did not. The Cl (2p_{3/2}) peak measured in the core

levels was observed at the binding energies of 199 eV for the TiO_{2-x}Cl_{2x}. Figure 2 shows the UV-Visible diffuse reflectance spectra of the TiO_{2-x}Cl_{2x} powders, TiO_{2-x}N_x powders and commercial UV photocatalysts, respectively. While TiO_{2-x}Cl_{2x} powders absorb at wavelength less than 520 nm, the TiO_{2-x}N_x powders absorb until at 600 nm in the visible range. TiO_{2-x}Cl_{2x} powders also showed faint absorption at wavelengths 600-700 nm, whereas references did not. Figure 3 shows half-lives of the reaction as function of sol temperature with TiO_{2-x}Cl_{2x}. Decreasing preparation temperature, the photocatalytic activity increased. This is due to crystallite size and is in accord with the results of the reference [4].

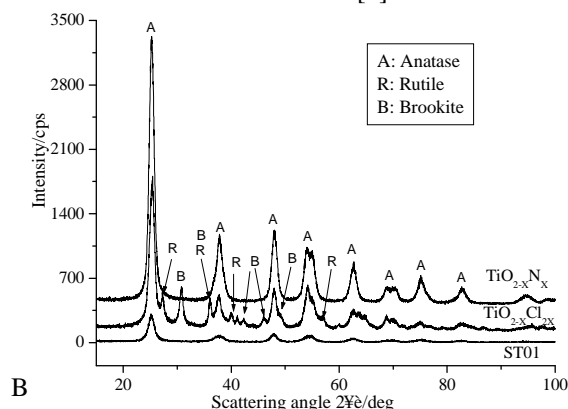


Fig. 1. X-ray diffraction pattern for TiO_{2-x}Cl_{2x}, TiO_{2-x}N_x and UV photocatalyst

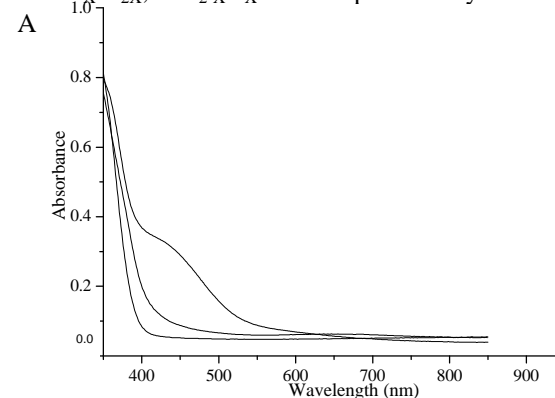


Fig. 2. UV-Visible diffuse reflectance spectra: (A) TiO_{2-x}N_x, (B) TiO_{2-x}Cl_{2x}, (C) UV photocatalyst

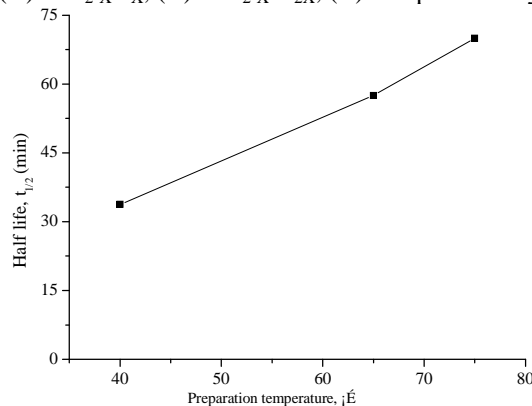


Fig. 3. Half-lives of the reaction as function of sol temperature : TiO_{2-x}Cl_{2x}

References

- [1] T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto, and S. Sugihara, *Appl. Catal. B: Environ.*, **42**, 403 (2003).
- [2] S. Sato, *Chem. Phys. Lett.*, **123**, 126 (1986).
- [3] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, *Science*, **293**, 269 (2001).
- [4] H. J. Nam, T. Amemiya, M. Murabayashi, and K. Itoh, *J. Phys. Chem. B*. In press.