-Communication-

Photocatalytic Degradation of Chloroform on Platinized TiO₂ Powder

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1 INTRODUCTION

It is well recognized nowadays that highly toxic and cancer-inducing chlorinated hydrocarbons are formed in drinking water during chlorine disinfection processes. Ollis et al. demonstrated for the first time that semiconductor photocatalysts are effective to remove these toxic organic compounds from water¹⁾ just like as other contaminants, i.e., CN⁻,²⁾ p-dichlorobenzene³⁾ and etc. For instance, they have shown that chloroform, CHCl₃, in water is totally decomposed into CO₂ and HCl using slurry of anatase TiO₂ illuminated with black-light fluorescent lamps; concentration of CHCl₃ was decreased from 100 ppm to 10 ppm within 3 h. Further investigation, however, is required particularly to increase the efficiency of the reaction.

In this preliminary experiment, we used rutile TiO₂ powder bearing in mind that its band gap is smaller than that of anatase form, and will be suitable for solar-driven systems. We show here that photocatalytic activity of rutile TiO₂ powder in the degradation reaction of CHCl₃ is largely enhanced by platinization.

2 EXPERIMENT

Figure 1 schematically illustrates the recirculating photoreactor used, which contains 1 l of water with 200 ppm CHCl₃ and 1 g of TiO₂ photocatalyst (300 mesh, Furuuchi Chemical Co., Ltd.). The light sources used are eight black-light fluorescent lamps (National FL20S, 20

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Fig. 1. Schematic illustration of the recirculating photoreactor. 1: quartz reactor, 2: black-light, 3: pump, 4: Teflon tubing, 5: sampling port, 6: magnetic stirrer, 7: temperature controller, 8: cooling fan.

W). This system is basically the same as that Ollis employed.¹⁾ The solution was sampled from the sampling port; concentration of chloroform and Cl⁻, and pH of the solution were measured using gas-chromatography, a Cl⁻ ion-selective electrode and a pH meter, respectively. The sampled solution was reinjected into the reactor after the measurements.

Pt was loaded onto TiO₂ powder by using the photodeposition method.⁴⁾ Four samples were prepared; Pt/TiO₂ ratios in weight % were 0, 2.5, 5 and 10.

3 RESULTS AND DISCUSSION

Figure 2 shows normalized concentration of CHCl₃ as a function of irradiation time for different amounts of loaded Pt. The decomposition rate tended to increase and the minimum concentration decreased as the amount of loaded Pt increased. In particular, chloroform disappeared almost completely after the irradiation time of 300 min for TiO₂-10 % Pt. The final concentra-

Fig. 2. Changes in normalized $[CHCl_3]$ as a function of time and the amount of loaded Pt under illumination.

tion was below the detection limit, i.e. several ppb. This shows that our system is more photoactive than that of Ollis et al.¹⁾ On the other hand, only 12 % of chloroform disappeared with bare TiO_2 (0 % Pt) in the same period. Thus, the loaded Pt largely enhanced the disappearance of $CHCl_3$. With several blank tests (e.g., without illumination), it was verified that this disappearance was induced by the photoexcitation of the TiO_2 photocatalysts.

In addition, a small amount of ethanol was observed during the illumination. This is consistent with that Ollis reported,¹⁾ and suggests a relatively complicated mechanism of the decomposition reaction of $CHCl_3$.

Rutile TiO_2 is reportedly less photoactive than anatase TiO_2 upon overgap irradiation.²⁾ This seems to hold also for the decomposition of $CHCl_3$ when compared the present results for bare rutile TiO_2 with those for bare anatase.¹⁾ However, rutile TiO_2 with 10 % Pt apparently showed even higher activity in comparison with anatase as a result of the enhancement due to the Pt loading. Although we are planning to examine possible enhancement with Pt for anatase TiO_2 and other semiconductor materials also, we can conclude at this stage that the combination of semicon-

Fig. 3. Photodecomposition of $CHCl_3$, and production of Cl^- and H^+ .

ductor photocatalysts having smaller bandgap energies and the Pt catalyst is very effective in the photodegradation reaction of $CHCl_3$.

Cl^- and H^+ will be accumulated in the reactor owing to the decomposition of $CHCl_3$.¹⁾ Final amounts calculated from the initial $[CHCl_3]$ (200 ppm) are 188 ppm for $[Cl^-]$ and pH 2.2 for H^+ . These values are much larger than those observed as shown in Fig. 3. Only the initial rate of the production of H^+ was comparable to the expected value. This is markedly different from the results in ref. 1, and may reflect differences between rutile TiO_2 and anatase TiO_2 in the reaction paths or in adsorption of the products. For instance, Cl^- can undergo successive oxidation, and H^+ can be adsorbed onto the surfaces of the rutile powder. Further examination is now under way.

References

- 1) D. F. Ollis, *Environ. Sci. Technol.*, **19**, 480 (1985), and references therein.
- 2) S. W. Frank and A. J. Bard, *J. Am. Chem. Soc.*, **99**, 303 (1977).
- 3) B. G. Oliver, E. G. Cosgrove and J. H. Carey, *Environ. Sci. Technol.*, **13**, 1075 (1979).
- 4) B. Kreutler and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 4317 (1978).