O U R N A L O F

Ceramic Processing Research

Characteristics of Ag photoadsorption by TiO₂ photocatalysts

Hae Keun Yoo, Dong Seok Seo^a and Jong Kook Lee^{*}

Dept. of Advanced Materials Engineering, Chosun University, Gwangju 501-759, Korea ^aSchool of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea

In this study, the photoadsorption properties of Ag ions in a AgNO₃ solution by a TiO₂ nano-powder synthesized by a homogeneous precipitation process at low temperature were investigated. It was found that the photocatalytic reduction in the AgNO₃ solution occurred by the TiO₂ nano-powder even under sun light irradiation, although the reduction of Ag ions was slow with a small adsorption of 9.32 ppm. Notably the Ag adsorption was promoted in dark conditions probably owing to the chestnut-bur shape of the TiO₂ nano-powder itself. With the application of UV the Ag ions were completely adsorbed within 120 minutes, showing a more significant photocatalytic reaction. The measured adsorption reaction rate and adsorption equilibrium rate constants were 0.0004 g/minute and 1494.20 (120 m²/g), respectively.

Key words: TiO₂, Ag, Photocatalytic reaction, Photoadsorption.

Introduction

Wastewater from photographic processing contains a high price in developing chemicals and valuable heavy metal ions such as silver. Recovering the metal ions from wastewater can be useful with respect to resource recycling and substitution with imported chemicals. As a discarded developing solution has a high concentration of silver (>6,000 ppm), a variety of silver recovery methods have been actively studied. In particular, a metal substitution method [1], an ion exchange method [2] and an electrolytic method [3] have been described. However, the metal substitution method has disadvantages in that not only are the substituted Fe ions released to the solution but also a high concentration of silver still remains in the solution. In the case of the ion exchange method, a secondary process for removing silver is necessary due to the presence of a mature microorganism, the presence of plastics and presence of tio-sulfate. In the generally used electrolytic method, 20 ppm of silver ions, which exceeds the permitted release level of silver ions (5 ppm), is outflowed.

Recently, interest has been expressed in TiO_2 photocatalyst as an alternative method for recovering metal ions from wastewater [4, 5] because this catalyst has chemical stability and good wear resistant, and a photocatalytic reaction can be produced by illumination of the sun or a fluorescent light. In this method, the reduction of metals is produced using electrons induced from the TiO_2 photocatalyst under illumination with uv-visible light. Herrmann *et al.* [4] have reported silver recovery from a low concentration Ag-containing solution and also silver separation from a Ag-Cu mixed solution using TiO₂ powder. Herrmann *et al.* used reagent grade Ag-containing solution for this silver recovery, while Huang *et al.* [5] has tested silver recovery from developing solutions due to the easy transmittance of uv-visible light. They found that silver was obtained in an approximately 3:1 ratio corresponding to the amount of TiO₂ employed and exceeding this ratio led to an efficiency recovery decrease because Ag lumps on the TiO₂ particles disturbed the transmittance of uv-visible light.

In this study, we utilized TiO_2 nano-powder with a rutile structure and investigated the silver photoadsorption ability of the powder in a reagent grade AgNO₃ solution. The photocatalytic results of the TiO₂ powder were also compared with the reaction conditions, such as light sources and oxic/anoxic conditions. The TiO₂ powder was produced by a homogeneous precipitation process at low temperature and has a large specific surface area and consisted of nano-sized primary particles with a chestnut- bur shape [6, 7].

Experimental Procedure

We evaluated the characteristics of silver photoadsorption of the TiO₂ powder with illumination conditions, such as sunlight, a dark condition and uv-visible light, and oxic/anoxic condition under UV irradiation. A cylindrical unit was used as the photocatalytic reactor with 0.2 g of TiO₂ and 2×10^{-4} M AgNO₃ solution (C_o=21.06 ppm, Ag ions). This was used for all experiments and 200 ml of AgNO₃ solution with dispersed TiO₂ particles was placed in the flask, followed by

^{*}Corresponding author: Tel:+82-62-230-7202

Fax: +82-62-230-7202

E-mail: jklee@mail.chosun.ac.kr

illumination with light.

For the photoadsorption experiment under sunlight, 0.2 g of TiO₂ powder in the AgNO₃ solution was dispersed with an ultrasonic device (Transsonic Ultrafine Cleaners, 460/H-Elma, Germany) at 35 kHz for 10 minutes and stirred for 30 minutes in a dark room, then the experiment was performed under sunlight. In the case of the experiment under dark conditions, the experiment was same as the case for sunlight, but it was performed in dark room. To investigate the effect of existing oxygen in the reactor on the photocatalytic reaction, the photoadsorption experiment was performed with oxic and anoxic conditions under UV irradiation, respectively. 150 ml/minute of nitrogen gas was continuously flowed into the reactor for the anoxic atmosphere and the experiment for oxic conditions was performed in air keeping the reactor open. The adsorption reaction rate and adsorption equilibrium rate constants were calculated from the amount of silver ions and the concentration of the AgNO₃ solution during the photocatalytic reaction.

The amount of adsorbed silver ions was measured from the silver concentration remaining in the AgNO₃ solution after taking 3 ml from the reacted solution at intervals of 10, 15, 30 and 60 minutes, followed by filtering the particles with an 0.2 μ m syringe filter, using atomic absorption (AA) spectrophotometer (Perkin-Elmer 5100 PC). The morphology of silver adsorbed on the TiO₂ particles was observed by transmission electron microscopy (TEM, JEOL-2000).

Results and Discussion

The crystalline phase and microstructure of TiO_2 prepared by the homogeneous precipitation process are presented in Fig. 1. The XRD patterns indicate that the TiO_2 powder had a rutile structure regardless of heat treatment temperatures. The TEM micrograph shows the mono-dispersed and chestnut-bur shaped TiO_2 ultrafine particles with diameters of 200-400 nm. The powders consist of needle-shaped primary particles with a width of 3-7 nm contributing to a large specific surface area of 180 m²/g [8].

Figure 2 shows silver concentration remaining in the AgNO₃ solution after reacting 2×10^{-4} M AgNO₃ solution with 2 g/l of TiO₂ under sunlight as a function of time. Although the adsorbed amount and rate of silver ion removal were small and slow at 9.32 ppm for 7 h, we have found that the TiO₂ nano-crystalline powder could induce a photocatalytic reaction even with sunlight containing only 5-10% of uv-visible light.

Under UV light irradiation and dark conditions, the change of silver concentration is presented in Fig. 3. When UV light was irradiated for only 120 minutes, the silver ions in the solution were completely adsorbed on the TiO_2 particles. On the other hand, the concentration of the adsorbed silver ions under the dark



Fig. 1. XRD patterns with calcined temperature (a) and TEM micrograph of rutile TiO_2 nano-crystalline powders (b).



Fig. 2. Ag concentration remaining in the aqueous AgNO₃ solution measured by AA spectrophotometer under sunlight.



Fig. 3. Ag concentration remaining in the aqueous $AgNO_3$ solution measured by AA spectrophotometer under dark conditions and UV light irradiation.

conditions was approximately 3.04 ppm, however the result indicates that silver adsorption occur not only by a photocatalytic reaction but also by an adsorption process. The silver adsorption without any light can be explained in terms of the properties of the powder used in this study. Since the TiO_2 powder consists of ultrafine needle-shaped particles with a large specific surface area, silver adsorption can occur not only by an oxidation reduction reaction of the photocatalyst [9] but also by the high adsorption ability of the powder itself.

To investigate the effect of the oxygen produced in the solution during UV light irradiation on the photocatalytic activity of the TiO₂ powder, the variation of silver concentration with N₂ gas purge (oxic) and no N₂ gas purge (anoxic) under UV light irradiation was evaluated and is presented in Fig. 4. Unlike the previous result [10] in which the photoadsorption property of the photocatalyst could be decreased due to a reduction between oxygen and electrons, the silver adsorption time and rate in this work were similar



Fig. 4. Ag concentration remaining in the aqueous $AgNO_3$ solution measured by AA spectrophotometer with N_2 gas purge (oxic) and no N_2 gas purge (anoxic) under UV light irradiation.



Fig. 5. TEM micrograph of the TiO_2 nano-crystalline powders after the photocatalytic reaction.

regardless of the presence of oxygen in the solution, indicating that the oxygen may have no effect on the photocatalytic reaction of the TiO_2 powder. It is suggested that the electrons generated from TiO_2 preferably reduce Ag^+ ions prior to a reduction reaction of oxygen and electrons, and therefore a little amount of oxygen in the solution can hardly affect the photocatalytic reaction of TiO_2 .

Figure 5 shows the morphology of TiO_2 powders after the photocatalytic reaction. Compared with the powder in Fig. 1(b), a large amount of reduced silver metal lumps were observed around the TiO_2 particles.

From the above results, it has been found that the silver adsorption at the early stage of the reaction proceeds rapidly and then the adsorption rate gradually slows. Subsequently little adsorption occurs up to the end of the reaction stage. This result can be assumed to be due to the reduced silver lumps which are adsorbed



Fig. 6. The linear appearance of plots of reciprocal initial concentration vs initial rate reciprocal verified the applicability of the Langmuir-Hinshelwood (L-H) rate form [11] to $AgNO_3$ solution.

around the surface of the chestnut-bur shaped TiO_2 particles which blocks other possible reaction sites inside the particles and decrease the reaction area and sites, resulting in a decrease in the amount of adsorption with reaction time.

In order to calculate the adsorption reaction rate and adsorption equilibrium rate constants using the adsorption reaction rate, the measured amount of adsorption of silver ions with concentration of AgNO₃ solution of 120 ppm is presented in Fig. 6. From these data, the measured adsorption reaction rate constant was 0.0004 g/minute and adsorption equilibrium rate constant indicating the possible area of silver adsorption, that is specific surface area was 1494.20 (120 m²/g).

Conclusions

The photocatalytic properties of needle-shaped TiO_2 powder with a large specific surface area were characterized by estimating the efficiency of silver adsorption in a AgNO₃ solution. We have found that silver adsorption by the photocatalytic reaction of TiO_2 powder occurred under sunlight irradiation even though the amount and rate of silver adsorption was small and slow. Under dark conditions, we also observed silver adsorption by the excellent adsorption ability of the chestnut-bur shaped TiO_2 powder. Under UV light irradiation, the powder showed the highest photoadsorption efficiency and a decrease of efficiency by recombination of electrons due to the existing oxygen was not observed. Many reduced silver lumps around the surface of TiO_2 particles was confirmed and the measured adsorption reaction rate and adsorption equilibrium rate constants were 0.0004 g/minute and 1494.20 (120 m²/g), respectively.

Acknowledgments

This study was supported by research funds from Chosun Univesity, 2002.

References

- 1. O.-J. Jung, H.J. Jung, and J.T. Kim, J. Kor. Chem. Soc. 32[4] (1988) 358-370.
- 2. D.A. Branch, J. Imag. Technol. 14[6] (1988) 160-166.
- 3. M. Chatelut, E. Gobert, and O. Vittori, Hydrometallurgy 54 (2000) 79-90.
- J. M. Herrmann, J. Disdier, and P. Pichat, J. Catalysis 113 (1988) 72-81.
- M. Huang, E. Tso, and A.K. Datye, Environ. Sci. & Tech. 30[10] (1996) 3084-3088.
- S.-J. Kim, H.G. Lee, S.D. Park, C.J. Jeon, C.K. Rhee, W.W. Kim, and H.G. Lee, J. Kor. Ceram. Soc. 37[5] (2000) 473-478.
- S.-J. Kim, S.D. Park, C.J. Jeon, Y.H. Cho, C.K. Rhee, E.G. Lee, and W.W. Kim, J. Sol-Gel Sci. Tech. 22 (2001) 63-74.
- S.-J. Kim, and S.D. Park, J. Kor. Inst. Met. & Mater. 39[2] (2001) 214-221.
- B.-M. Lee, and D.Y. Shin, J. Kor. Ceram. Soc. 37[4] (2000) 308-313.
- K.-S. Jung, and H.I. Lee, J. Kor. Chem. Soc. 41[12] (1997) 682-710.
- 11. C.S. Turchi, and D.F. Ollis, J. Catalysis 119 (1989) 483-496.