

Discharge photoelectrocatalytic system for the degradation of aromatics

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ABSTRACT. We have introduced the discharge photoelectrocatalytic system, in which TiO₂ thin film coating on aluminum plate is subjected simultaneously to both UV irradiation and high voltages in excess of 3000 volts. Due to high voltages O₃ is generated; however, efficient removal of O₃ is observed in this photoelectrocatalytic system. In terms of the removal of volatile organic compounds (VOCs), the discharge photoelectrocatalytic system has been applied to the removal of aromatic compounds such as benzene and toluene. Based on the experimental data, the rates of the removal of these compounds in this system are higher compared to either the discharge-only system (without the photocatalyst) or the photocatalyst-only system (without high voltage discharge), and the higher rates of degradation of these compounds in the photoelectrocatalytic system are attributed to the reduced rate of electron-hole recombination in TiO₂.

1. INTRODUCTION

Much attention has been given to titanium dioxide (TiO₂) due to its outstanding photocatalytic properties such as photochemical stability and high oxidation rates. Nevertheless, its industrial applications such as removal of pollutants [1, 2] in the industrial sites and wastes have been slow due to the limitations associated with the requirement of UV light for the generation of excited electrons and holes and their subsequent rapid recombinations [3, 4].

The discharge photoelectrocatalytic system was recently designed in this group for the purpose of increasing the photocatalytic activity by trapping electrons generated in TiO₂ upon UV irradiation, and this system was used for the removal of aromatic compounds such as benzene and toluene. The discharge photoelectrocatalytic system maximizes the photocatalytic activity by retarding electron-hole recombination, thereby increasing the lifetime of holes responsible for the mineralization of these compounds. In the discharge photoelectrocatalytic system, the degradation rates of these compounds increased with the increase in the applied voltage on the aluminum plate. Overall, the degradation rates of these compounds were higher under the condition of simultaneous UV irradiation and applied voltage in comparison to the conditions of either UV irradiation only or the applied voltage only. Our discharge photoelectrocatalytic system also demonstrates generation and consumption of ozone (O₃), which are due to the discharge effect and the photocatalytic effect, respectively [5].

2. EXPERIMENTAL

The photocatalyst used in this study was sol type titanium dioxide (Enpion, Korea; 15% TiO₂) suspended in alcoholic solvent, which will be referred to as Enpion TiO₂. Enpion TiO₂ was mixed with silicon binder solution (silicon, alcohol, water, acid) of pH 3.5 to increase the coherence of titanium dioxide on the substrate, aluminum plate. Evaporation of the solvent followed by drying at 80 °C for 4 hours and shredding turned the Enpion TiO₂ into powder for the BET and XRD measurements. Surface area analysis was done using ASAP 2010 (Micrometric Science) and structural measurement by X ray Diffractometer (Rigaku D-Max 2200). For the XRD measurement Cu K α radiation was used, and the sample scans were collected between 8° and 20° 2 θ . The Enpion TiO₂ powder sample was viewed by Jeol JSM-6400 scanning electron microscope (SEM).

Aluminum plate was coated with Enpion TiO₂ using a bar-coater, which was dried at 120 °C for 30 mins in the air without calcinations. TiO₂ coated aluminum plate was then used as a cathode for the discharge photoelectrocatalytic system and an array of Cu strips in the shape of saw tooth was used as an anode (Figure 1). High Voltage DC bias was used for the discharge in the system, and voltages of 3000 volts and 5000 volts were applied to observe the effect of the electric field on the photocatalytic activity. Three 8 W UV lamps (GLK8CQ, Sankyo Denki) were used for the irradiation of TiO₂ coated aluminum plate.

Air flowed through a mass flow controller into the saturator placed in a constant temperature bath at 20 °C and 1 atm, and was mixed with 90% air coming from another mass flow controller in order to obtain

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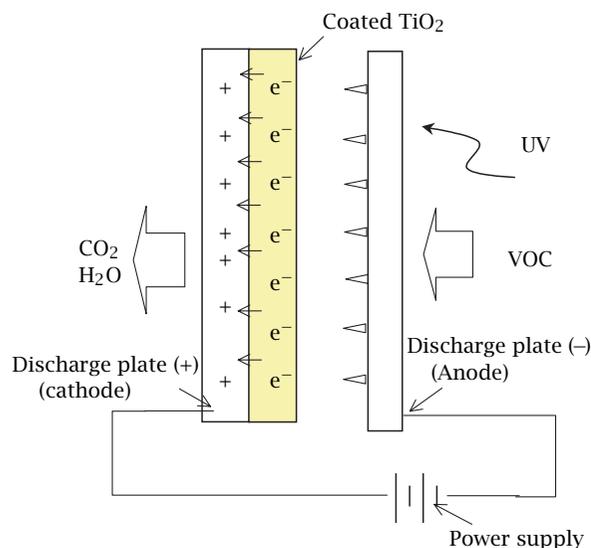


Figure 1. Schematic diagram of the discharge Photoelectrocatalytic System.

1 vol.% aromatic compound in air. This aromatic mixture flowed into and out of a 10l batch reactor initially, to allow adsorption to take place in the reactor, and samples of outlet mixture were periodically analyzed with a gas chromatograph (HP6890) equipped with a flame ionization detector and a capillary column (HP5) to be compared with the target composition. When the target composition of 1 vol.% was achieved, the inlet and outlet of the reactor were closed, and photoelectrocatalytic degradation of the aromatic compound was carried out in this batch reactor at 20 °C and 1 atm. During the experiment gas samples were taken at 30 min. interval for GC analysis to monitor variations in the concentration of the aromatic compound.

3. RESULTS AND DISCUSSION

Surface area analysis results for Enpion TiO₂ are presented in Table 1 along with the results for the reference compound (P-25 TiO₂). BET measurements in Table 1 reveal that the specific surface area of Enpion TiO₂ is ~ 5 times larger than P-25.

The XRD patterns for the photocatalysts in Figure 2. showed that only anatase existed in Enpion TiO₂. On the other hand, the reference compound (P-25 TiO₂) showed both anatase and rutile crystallinity.

Table 1. Specific surface areas and pore volumes of P-25 and Enpion TiO₂.

	BET(m ² /g)	Mean Pore Size (Å)	Total Pore volume (cm ³ /g)
P-25	55.15	131.84	0.14
Enpion	275.24	40.8	0.25

SEM images of Enpion TiO₂ with and without binder as well as those of P-25 TiO₂ are shown in Figure 3. The particles in Figure 3(b) are larger than those

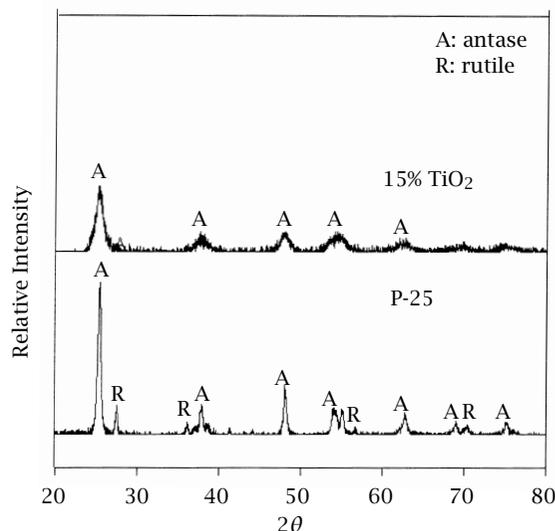
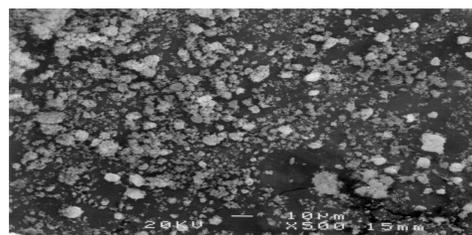
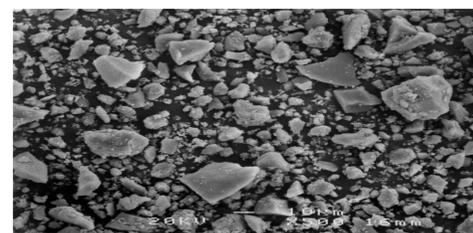


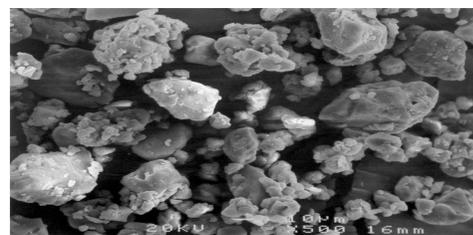
Figure 2. X-ray diffraction patterns for P-25 and Enpion TiO₂.



(a)



(b)



(c)

Figure 3. SEM photographs (×500) of various powers: (a) P-25, (b) Enpion TiO₂, (c) Enpion TiO₂ with the binder.

in Figure 3(a), showing signs of aggregation. Significant increase in the size of the particles is seen in Figure 3(c) due to clustering, and this clustering might have been accelerated by the silicon binder. These clusters are expected to provide a highly porous morphology [2, 3], and this agrees with the large BET values for Enpion TiO₂.

Figures 4 and 5 show the degradation of the aromatic compounds as a function of UV irradiation time for the three cases of operating conditions: (a) discharge only (plasma effect), (b) UV irradiation only (conventional photocatalytic effect) and (c) discharge with UV irradiation (photoelectrocatalytic effect). In the figures, the dot symbol corresponds to the condition (a), the circle to the condition (b), and the reverse triangle to the condition (c). For both benzene (Figure 4) and toluene (Figure 5), the degradation rate of case (c) was significantly higher than either case (a) or case (b), showing the highest catalytic activity. Between the case (a) and the case (b), the degradation rate of case (b) was slightly higher than that of case (a).

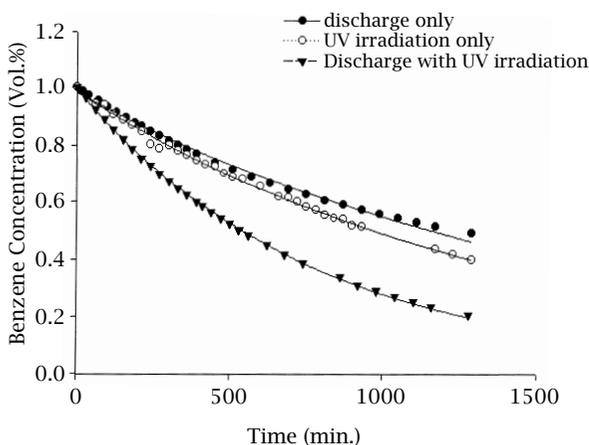


Figure 4. Photodegradation of benzene as a function of UV irradiation time.

The curves in Figures 4 and 5 are the best fits to the experimental data up to 1300 mins. using a single exponential decay model. Based on the high quality of the fits, pseudo first order rate constants are applied to the degradation of benzene and toluene for the purpose of comparison. The rate constants for the cases (a), (b), and (c) in benzene are 5.65×10^{-4} , 6.97×10^{-4} , and $12.41 \times 10^{-4} \text{ min}^{-1}$, respectively. Thus, under the photoelectrocatalytic effect benzene decomposed ~ 2.2 times faster than under the plasma effect only and ~ 1.8 times faster than under the photocatalytic effect only. In toluene, the rate constants for the cases (a), (b), and (c) are 1.83×10^{-4} , 3.97×10^{-4} , $8.89 \times 10^{-4} \text{ min}^{-1}$, respectively. Accordingly, toluene under the photoelectrocatalytic effect decomposed ~ 4.9 times faster than

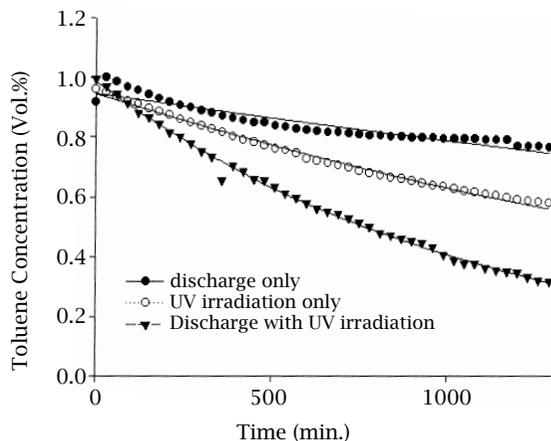


Figure 5. Photodegradation of toluene as a function of UV irradiation time.

under the plasma effect only and ~ 2.2 times faster than under the photocatalytic effect only.

An explanation for the highest degradation rate of the case (c) can be found in the trapping of the photogenerated electrons, and such an effect would retard electron-hole recombination, thereby increasing the lifetime of the holes capable of mineralizing benzene into carbon dioxide (CO₂) and water (H₂O).

As to the difference in the degradation rates between the case (a) and the case (b), it is more pronounced for toluene than for benzene, and this observation may have to do with the fact that toluene has nonzero dipole moment (~ 0.33 debye). In the presence of the electric field, toluene molecules are likely to align with methyl groups pointing toward the Cu strips; however, such an orientation might have resulted in adverse effect in our experiment.

The effect of voltage on the degradation of the aromatic compounds in the discharge photoelectrocatalytic system is shown for benzene in Figure 6. In the figure the circle corresponds to the benzene

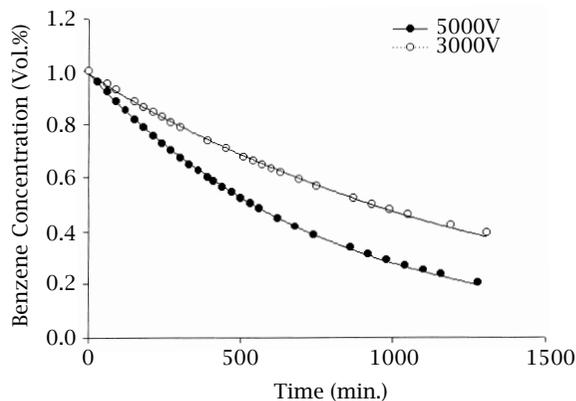


Figure 6. The effect of applied voltage on the photodegradation of benzene.

concentration under the discharge of 3000 volts, and the dot symbol corresponds to that of 5000 volts, and the curves represent a single exponential decay fit to the data. As shown in the figure, the benzene degradation rates were higher with higher applied voltage on the aluminum plate. In terms of the pseudo first order rate constant, it is $12.41 \times 10^{-4} \text{ min}^{-1}$ at 5000 volts and $7.2 \times 10^{-4} \text{ min}^{-1}$ at 3000 volts. Based on this result we suggest that higher electric field induces larger number of trapped electrons on the aluminum plate and the stronger plasma effect, thus leading to higher rate of degradation of benzene.

The generation and the removal of ozone (O_3) in the discharge photoelectrocatalytic system are shown in Figure 7. As shown in the figure, ozone (O_3) produced in the discharge system could be removed by UV irradiation onto TiO_2 , which was demonstrated by a dramatic decrease in ozone concentration immediately following irradiation of UV light.

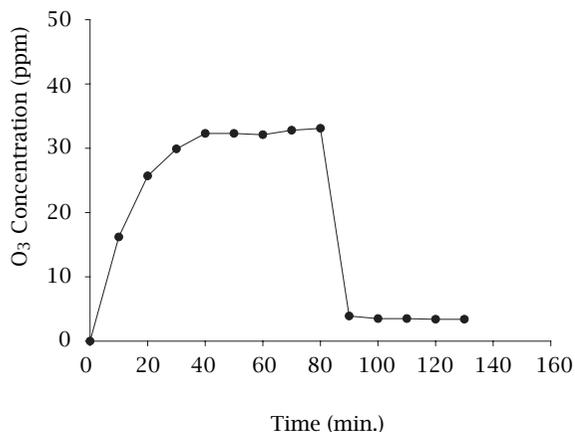


Figure 7. Generation of O_3 by the plasma effect and its removal by the photocatalytic effect in the discharge photoelectrocatalytic system.

Recently, the plasma system as well as the electrostatic precipitator based on the discharge system are being launched as advanced air cleaning system. However, in both cases, the amount of ozone drawn out of the air cleaner is not negligible, and it can be potentially harmful for people in the confined space over extended period of time. The discharge photoelectrocatalytic system will be an answer to such health hazardous problems.

4. CONCLUSIONS

The degradation of benzene and toluene was carried out in the discharge photoelectrocatalytic system consisting of TiO_2 thin film, its aluminum substrate as cathode, anode of Cu strips, high voltage power supply and UV lamps. Compared to either the plasma effect only or the photocatalytic effect only, higher degradation rates were observed for both benzene and toluene in the discharge photoelectrocatalytic system. In terms of the effect of the voltage on the degradation of the aromatic compounds, higher degradation rate at higher applied voltage was observed for benzene. Between benzene and toluene, degradation of benzene was faster than toluene in the discharge photoelectrocatalytic system, and benzene decomposed ~ 1.4 times faster than toluene based on the pseudo first order rate constants. The higher rates of degradation for these aromatic compounds are attributed to the longer lifetime of holes in TiO_2 due to reduced electron-hole recombination.

The discharge photoelectrocatalytic system produces ozone by the plasma effect due to the high voltage discharge. However, ozone is consumed photocatalytically upon production within the system, and therefore, the amount of O_3 coming out of the discharge photoelectrocatalytic system is quite low. Compared to the UV lamps, the discharge photoelectrocatalytic system consumes little amount of electricity (2-4W), and thus has the advantage of being energy efficient.

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