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광촉매가 코팅된 플라스틱 광섬유을 이용한 VOC 광분해반응

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Photodegradation of VOCs by Using TiO_2-Coated POF

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Abstract In this study plastic optical fibers (POFs) were considered as light-transmitting media and substrates for the potential use in photocatalytic environmental purification system. After the characteristics of POFs in terms of light transmittance and absorption were determined at the beginning, the further investigation was performed through the photocatalytic degradation of trichloroethylene (TCE), iso-propanol and etc. with TiO_2-coated optical fiber reactor systems (POFR). It is concluded that the use of POFs is preferred to quartz optical fibers (QOFs) since the advantages such as ease of handling, lower cost, relatively reasonable light attenuation at the wavelength of near 400nm can be obtained. Various geometrical reactor shapes have been constructed and applied for the last one and half years. For the use of POF in water phase treatment, however, more detailed scientific and engineering aspects should be envisaged. This case requires a suitable mixture to obtain more stable and innocuous immobilization of photocatalyst on POF. To overcome this disadvantage, metal-organic chemical vapor deposition (MOCVD) was conducted in a fluidized bed to deposit thin films of titania on glass and alumina beads. Those can be used as photocatalysis for the removal of pollutants especially in liquid phases.

1. Introduction

Environmental remediation using photocatalyst has been the most intriguing issue in many countries for the past decade. While various research areas on photocatalysis have been studied, the immobilization of photocatalyst on a specific substrate, in particular, has received considerable attention due to the versatility of application. In this study, plastic optical fibers (POFs) were considered as light-transmitting media and substrates for the potential use in photocatalytic environmental purification system, comparing with that of quartz optical fibers (QOFs). It is concluded that the use of POFs is preferred to QOFs since the advantages such as ease of handling, lower cost, relatively reasonable light attenuation at the wavelength of near 400nm can be obtained. And also, this system has been identified to achieve two main goals; transfer of light and volumetric reaction among the various immobilized reactor system. In the mean while, the POF system is not quite eligible for the abatement of harmful organics in water due to its lack of stability in water. Fluidized bed has been utilized for several decades in many chemical and environmental industries [1]. One of the most potential processes is fluidized bed Chemical Vapor Deposition (CVD) [2]. In this paper, a circulating fluidized bed (CFB) is operated under vacuum and high temperature conditions. We perform deposition of TiO_2 coatings on small glass beads in a circulating fluidized bed reactor for the use of photocatalyst and discuss the results of hydrodynamics. Photocatalytic activities of the titania/glass bead particles will be discussed in future work.

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2. Theory

The incident light on one end of fiber transmits to the other end by total reflection if clad (made of fluorinated PMMA, F-PMMA) exists which has lower refractive index than core. Once the clad is peeled off and then photocatalyst is coated on the surface of the fiber, refracted light can be absorbed due to higher refractive index of photocatalyst than that of core material. The core of the optical fiber can be made of quartz or polymer (mostly polymethyl methacrylate, PMMA). The former has relatively lower light attenuation (102~1 dB/km at the range of 300~800 nm), but it is very difficult to handle and its cost is expensive. For this reason plastic optical fibers (POFs), which are inexpensive, flexible, resilient, tough, and weather resistant at temperature range of 55~70°C, were chosen to achieve the same goals of OF systems and resolve the aforementioned problems of the QOFs simultaneously. Using POFs in photocatalytic system can be promoted by the fact that the light attenuation difference hardly affects the reactivity in such a short length of transmittance and solar light and UV-A lamp in the absence of light <300 *nm does not degrade POFs' core structurally.* In CFB process, each particle is coated with a thin film of a new material, thus changing the properties of particles. Its main applications cover the improvement of catalytic activity, the deposition of diamond coatings on particles, and the production of ultra pure silicon for solar cell. Especially, this process makes it possible to uniformly coat small, three-dimensional objects such as powders, fibers, and small pieces of equipments. It is difficult to do with conventional chemical vapor deposition methods, because entire surface area is not come out to the activated gas. This process, hence, can be an excellent choice to obtain extremely stable TiO_2 immobilization.

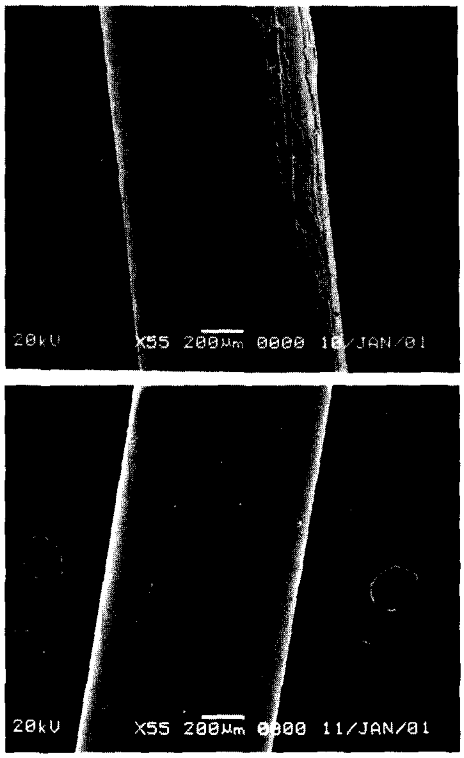


Figure 1. SEM of treated POF in acetone for 30 sec (top, wrinkled clad layer shown) and for 5 min (bottom, clad removed clear surface shown).

3. Experimental

Pretreatment of POFs could not be done either thermally or physically because the materials of core and clad is very similar to each other. Solvation using appropriate solvent was finally chosen to remove the clad of POF. After removing the clad from POF with 1mm diameter, the resulted diameter should be close to 0.98mm(matched with data by supplier). Clear proof of change in diameter of the POF was obtained by SEM (JSM 5900, JEOL) taken at various time scales (Figure 1).

Figure 2 shows the CFB of a SUS tube (40 mm i.d. and 0.5 m height). The fluidizing gas is supplied to the bottom of the riser. The particles leave the riser through a horizontal tube at the top, and are separated from the gas in a cyclone. They are recirculated to the riser through down comer and L-valve. The gas exit of the cyclone is linked to the vacuum unit. A total mass of 200 gm glass bead particles was handled per batch. In this process, thermal CVD was used to deposit thin films of TiO_2 on glass and alumina beads. Mixtures of argon, oxygen and titanium tetraisopropoxide (TTIP) were fed as reaction gases at reduced pressures. Temperature and pressure were measured with thermocouples and pressure sensors. The process pressures were measured above and bottom of the riser. In the thermal CVD of thin TiO_2 films, TTIP is decomposed in the fluidized bed and react with oxygen on the surfaces of glass and alumina beads.

Selection of chemicals to immobilize photocatalyst on the surface of stripped optical fiber was main research topic in using POFs. For about two years of trial, suitable binder-like chemical (we call it "**SM**")

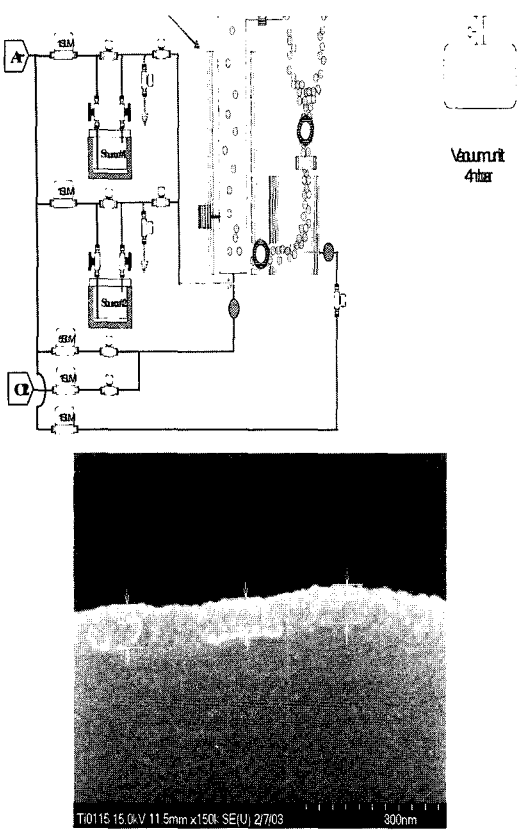


Figure 2. Schematic of CFB-CVD and FE-SEM image of TiO_2/glass bead..

has *recently* been identified and under investigation in terms of stability, light characteristics, harmfulness, etc. (Figure 3). In addition, reactors of various

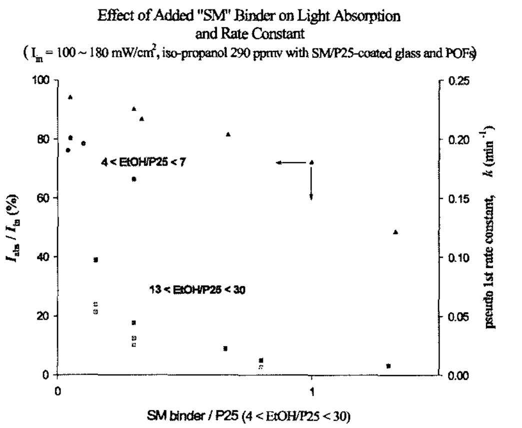


Figure 3. Effect of added "SM" binder on light absorption and rate constant (iso-propanol 290 ppmv in 650ml reactor).

shapes (cylindrical, rectangular, filter-type etc.) have been designed and tested using a couple of probe materials to obtain promising results that support superiority of this POF system. Light sources were a 1 kW Xenon lamp (from Oriel) and UVBLBs with different size (output power). Gas chromatograph (GC w/electron capture detector and mass selective detector, Hewlett Packard 5890) and FTIR were main tools for analysis.

4. Results and Discussion

Before performing various experiments, light transmittance characteristics of QOF and POF were investigated and compared qualitatively [3]. In the case of POF the amount of light transmitted was lower than in QOF and also in particularly light with a wavelength less than 300nm can not be transmitted via POF. This range of light is to be absorbed by PMMA, will structurally degrade PMMA. While the stripped fiber has lower light transmittance ability due to refraction at the exposed surface, the coated fiber has much lower transmittance with increasing coating times due to the light absorption by TiO_2. The effect of POF diameter, coated thickness, number of fibers, and length of fibers has been identified and used as basic data for further engineering design. A gas chromatograph and FTIR study showed that reaction byproducts, which actually proved that photocatalysis happened in POF system. To check the feasibility of POF in solar-driven photocatalytic system [4] that degrade low concentrated gas phase noxious chemicals, e.g. volatile organic chemicals and odorants, experiments to convert isopropanol (IPA) were conducted and result is shown in Figure 4. Acetone was produced while IPA had been converted with unidentified by-product shown. The conversion rate got faster when the reaction was performed repeatedly. This is due to the increasing exposure of activated surface of photocatalyst. So far, five POF reactors with different size have been prepared. Rectangular reactor has volume of 2,366 cm^3 (36.4 cmx6.5 cm and 10cm in height (H)) with TiO_2-coated area of ca. 3,600 cm^2. This reactor includes 900 POFs (1.5 mm in diameter (D) and 10 cm in length (L)) and gets 350 ppmv of trichloroethylene (TCE) converted within 10min with good reproducibility. TCE was completely degradation into CO_2 (by FTIR) and by-products identified by a gas chromatograph were acetaldehyde, formaldehyde, and acetic acid. A gas chromatograph and FTIR analysis was well matched in terms of time when by-products and CO_2 were generated. Radial reactor has volume of 4,973 cm^3 (outer D 8.52 cm, Inner D 2.52 cm, H 24 cm) with TiO_2 coated area of ca. 3,000 cm^2. This reactor is filled with 1,280 POFs (1.5 mm in diameter and 5cm in length). In this reactor 250~1,000 ppmv of methyl tert-butyl ether (MTBE) was converted in 10~30 min. MTBE was mineralized into CO_2 with molar ratio of one to five. Within 10 minutes after the reaction initiated the first byproduct, tert-butyl formate (TBF), has appeared drastically followed by acetone. Acetone was also major component among several byproducts in our experiments. This result was also verified by the fact that photocatalytic degradation of TBF and tert-butyl alcohol (TBA) as a starting material, producing acetone commonly. These reactors have been tested and modified in a way of easy handling, excellent light-utilizing ability and high rate constant. As previously mentioned, reaction rate is much higher when binder component is not used. Hence, when high rate is necessary, the use of photocatalyst-sol without binder in designed filter-shape reactor would be another possibility. Cylindrical reactor attached to a solar tracker (EPPLEY Lab.

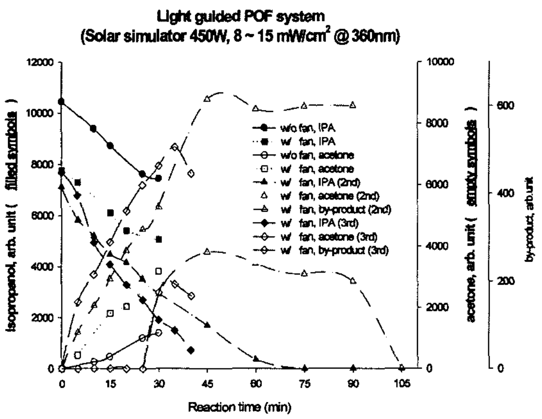
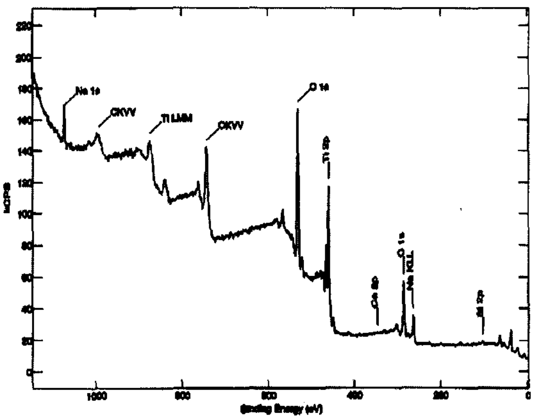


Figure 4. Isopropanol (IPA) conversion (top) with the light guided reactor (bottom) (Solar simulator, 8~15 mW/cm^2 @ 360 nm, IPA 290 ppmv).



elements	at %
Na	4.78
O	45.02
Ti	14.28
Ca	0.12
C	34.03
Si	1.77

Figure 5. XPS result and surface composition of titania coated glass beads.

Inc., USA) is prepared for the possible use of POF in sustainable air purification. This contains twelve POFs in 650 cm^3 where 350 ppmv of TCE was converted in 60 min. Finally, bundled array with 130 POFs each of which is 2 m long and only 20cm is coated has been prepared. This reactor is with both solar concentrator to increase light intensity and water filter to prevent POF from melting.

The chemical composition on the coated glass beads was identified with X-ray photoelectron spectroscopy (XPS). As can be seen in Figure 5, it shows a TiO_2 content of 59 at.%, with the main impurity being carbon (34 at.%).

The high content of carbon may be due to the high precursor concentration. X-ray diffractometer (XRD) was used to detect the anatase and rutile crystallite phase of titania. The XRD pattern of titania coated glass beads is shown in figure 6. It is found that the portions of anatase and rutile are 65% and 34%, respectively.

5. Conclusions

The use of POF in photocatalysis with an appropriate light source turned out promising in terms of high efficiency and widened fields of application. Eventually, the difference of reactivity between POF and QOF was negligible under our conditions. Various light sources could be used with POF because they do not irradiate light with wavelength shorter than 300 nm. The low cost of raw material and fragility also enhanced the versatility of POF system. Metal-organic chemical vapor deposition(MOCVD) was conducted in a fluidized bed for the preparation of titania nano-coatings on glass beads. For the characterization of TiO_2/glass beads, FE-SEM/EDXS, XPS, UV spectrophotometer and XRD were used to confirm nano-coating of titania, chemical composition on particle surface, photocatalytic activity with methylene blue, and crystallinity of titania.

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