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Photocatalytic degradation of 4-chlorophenol in a photochemical reactor with an interconnected microchannel and a light guide network

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ABSTRACT

Photocatalytic microchannel reactor with a novel light guide of fused glass beads was developed. Anatase nanoparticle photocatalyst was deposited on the inner surface of the porous glass monolith of the reactor. Activity of the reactor was evaluated based on photocatalytic degradation of 4-chlorophenol. All the glass beads in a glass column were fused with each other and with the inner peripheral of the column to form a glass network, which construct a network of light guide to deliver the incident light from side wall to each bead in the column. In contrast, almost all the voids among the beads connect with each other to form a network of microchannels for substrate solution, where many parallel flow of the substrate solution can pass through the reactor. Microchannel reactors composed of 5 mm or 1 mm glass beads in diameter were investigated, so that the dimension of the channels are evaluated as approximately 750 μm and 150 μm, respectively. The glass web monolith serves as a support of TiO_2 photocatalyst and a light guide to deliver the incident light to activate the photocatalyst on each bead. Photocatalytic activity of the reactor constructed with the 1 mm or the 5 mm glass beads was improved 13 and 3 times as much as that of the simple glass column without the beads, respectively. The ratio in the reactivity was proportional to the ratio in internal surface area of the reactors, supporting the effect of the glass web as light guide and the network of the voids as microchannel.

1. Introduction

Micro flow photochemical reactors with micro/nano channels have been focused in synthetic organic chemistry in recent years [1,2]. Characteristic channel size of the micro flow reactor is typically in the order of several hundreds of micrometers, resulting in the high surface area to volume ratio, laminar flow and mixing by diffusion, rapid control of reactor temperature, facilitates their application to synthetic organic chemistry [3,4]. Short optical path length permits homogeneous irradiation throughout the reaction field, which enables wide application of photochemistry as key steps in organic synthesis; oxidation [5], reduction [6], cycloaddition of olefins [7,8], addition of alcohol [9], redox reaction of alcohol [10], and Barton reaction [11]. Studies on kinetics of photocatalytic degradation of model pollutants in microchannel reactors revealed that mass transfer and photon flux can be the rate limiting steps [12] with exception under very slow flow rate in the order of $\mu L\ min^{-1}$ for each channel [13]. The reaction condition can be suitable for synthesis of products and intermediates of high price, such as medicine or speciality chemicals. However, significant scaling-up will be required for bulk reactions, such as water purification or solar to chemical energy conversion systems [14,15]. According to these studies, requirement for scaled-up photochemical microchannel reactor will be parallel micro channels to flow a large volume of substrate solution, large surface area to deposit much photocatalyst and efficient optical guide to deliver irradiation light to each photocatalyst in the reactor.

Photocatalytic reaction system with parallel flow microchannels have been reported using Teflon tubing, optical fibers and beads. Teflon tubing is a cost competitive material, so that parallel channel is also available for scaling-up organic synthesis [16]. Dimension of the tubing is in the order of several hundred micrometers in inner diameter and several meters in length, which permits long residence time for irradiation. However, risks for fouling by solid precipitation or clogging by gaseous products should be considered for practical application. Optical fiber bundle on which photocatalyst was deposited was reported as elegant

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photocatalytic reactors [17,18]. The optical fiber serves as light guide to deliver the excitation light to the photocatalyst deposited on the surface of the fiber. Incident light coming from the edge of the fiber transfers in the fiber and partly leaked to the clad for excitation of the photocatalyst layer due to higher refractive index of the photocatalyst than the glass core. But the small window of the incident light will cause a shortage of light for scaling-up by elongation of the fiber, then the application is limited to gas or diluted solutions.

Porous aggregates of beads supports have been reported as prospective candidates for bulk photocatalytic reactors [19–24]. Voids surrounded among the beads of 5 mm in diameter will be in the order of several hundreds of micrometers, and the voids are connected with each other to form a set of parallel flow channel for substrate solution. The parallel channel will be suitable to close contact of the substrate on the photocatalyst and to robust channel network to avoid fouling or clogging in principle. Ceramic beads of ca. 6 mm in diameter coated with photocatalyst were fixed on a large disk holder, which rotate slowly to convey the ball in and out of the substrate solution to make laminar flow on the beads [19]. Fixed bed system with stacks of beads support were irradiated under a flow of substrate solution [20]. Surface area of the beads support can be easily expanded by reducing the size of the component beads of 1 mm in diameter [21]. Soda-lime glass beads of 124 μm in diameter can form photochemical reactor with much higher surface area and smaller channels in the order of several tens of micrometers [22]. A fluidized bed containing the microbeads coated with TiO_2 photocatalyst was irradiated with UV-lamp to decompose oxalic acid as a model pollutant. The fluidization can make the beads and the solution homogeneously mixed to prevent accumulation of the solution in the voids. Microbeads support coated with complete coverage of photocatalyst layer was stable under hard collision in the operation of fluidized bed reactor [23,24]. All of the beads support described above were coated with photocatalyst layer, therefore the photocatalyst must be irradiated from the surface of the beads. When the beads are stacked or aggregated, only the beads located on the most outer surface of the aggregate can be irradiated and activated to generate hole and electron pair. Beads located underneath the surface layer should be left in the shade of the beads located at the surface layer. Beads located in the aggregate apart from the surface layer will be left in the dark and far from their activated state. The situation will be much severer for smaller beads support. Vigorous mixing of the beads in fluidized bed reactor will be insufficient to deliver the excited photocatalyst throughout the reactor, considering the lifetime of the excited state of photocatalyst in general.

Porous monolith with strait channel can introduce the incident light through the porous reactor, in addition to an efficient flow of the substrate gas [25]. Optimal size of the micro-pore for introduction of incident light and efficient flow of gaseous substrate was reported as ca. 1 mm squared. Unfortunately, the penetration length of the incident light into the monolith reactor with 1 mm channel was as long as 20 mm form the edge of the opened pores, though a collimated lamp was aligned just in front of the pore [26]. These reactors reported to date equipped wide surface area to deposit photocatalyst, narrow channels for close contact of substrates on the photocatalyst. If they prepare for independent optical guide to deliver incident light from the side wall of the each photocatalyst deposited on the inner surface of the columnar reactor, they will be an example of an ideal photocatalytic reactor.

In this paper, a novel photocatalytic reactor with optical light guide of porous glass monolith. The porous glass monolith was made of glass beads filled in a glass column. All the glass beads are fused with each other and the beads in contact with the inner surface of the column are also fused to the inner surface to fabricate a porous monolith like a glass frit filter. The porous glass network can serves as light guide to deliver the incident light from the side wall of the column onto each photocatalyst deposited on the inner surface in the reactor. In contrast, the voids surrounded by adjacent beads of 5 mm or 1 mm in diameter forms a micro channel for substrate solution. The porous monolith glass reactor with wide inner surface area and narrow flow channel has been equipped an independent glass web to deliver the incident light onto each photocatalyst. The performance of the reactor was evaluated based on an efficiency in photocatalytic degradation of 4-chlorophenol (4CP).

2. Materials and methods

2.1. Materials

A reference anatase powder ST-01 from the Catalysis Society of Japan was used as a standard sample of anatase and a reference sample of rutile was purchased from Wako Pure Chemicals. Anatase nanoparticle paste (PST-18NR, JGC Catalysts and Chemicals Ltd.) was used as received. 4-Chlorophenol, acetone, ethanol (Special Grade, Wako Pure Chemicals) were used as received. Potassium ferrioxalate was synthesized and used as chemical actinometer [27].

2.2. Microreactor system deposited with anatase TiO_2 nanoparticles

Borosilicate beads (d = 1 mm and 5 mm) were purchased from Ohashi Steel Ball, Co. A borosilicate pipe, 30 mm in outer diameter, 27 mm in inner diameter and 500 mm in length, was filled with the borosilicate beads and calcined to be a porous monolith, in which each beads were fused with adjacent beads or inner surface of the column. The calcination process were carried out in Tobita Scientific Glass, Co. On both ends of the columnar reactor was fit an inlet and an outlet pipe of borosilicate. Number of beads filled in the reactor was evaluated by weighting the reactors with or without beads and dividing it by the weight of each bead. The reactor volume was estimated by comparing the weight of the reactor filled with water and the vacant ones.

The columnar reactor was washed with nonionic detergent, rinsed with distilled water and filled with conc. H_2SO_4-30% H_2O_2 aq. mixed solution (1/1 (v/v)) overnight to make the inner surface hydrophilic. The column was washed with a volume of distilled water, rinsed with methanol, and dried under air flow. A paste containing anatase nanoparticles (12 g, PST-18NR, JGC Catalysts and Chemicals Ltd.) were mixed with ethanol (48 g) to prepare stable dispersion of anatase nanoparticles. The column was filled with the anatase dispersion, kept for 30 min, then the excess dispersion was ejected. The slightly opaque column was dried under air flow and calcined at 450 °C for 2 h. Hardness of the anatase coating was measured by the method of JIS K 5600-5-4 pencil hardness test, using a Cotec KT-VF2391 measurement jig.

2.3. Instruments

Microscopic photograph was observed using an digital optical microscope (AnMo Electronics Dino-Lite Pro). A Rigaku RINT system was used for XRD measurement (Cu, Kα, 40 kV, 150 mA). Uv–vis. spectra were measured on a Shimadzu UV-2400PC spectrometer. Photon flux of black-light lamp was measured using an Ushio UTI-201 power meter using an UVD-S365 sensor. Product distribution was analyzed by HPLC using a JASCO UV-875 detector, monitoring the absorbance at 255 nm. The column was a GL-Science Inertsil-NH2 (5 μm silica beads support, 4.6 mm x 260 mm) using a mixture of methanol/water/acetic acid (50/50/1, volumetric ratio) at flow rate of 1 mL min^{-1}. Cyclic voltammetry