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Design and evaluation of photocatalytic micro-channel reactors using TiO_2-coated porous ceramics

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Abstract

Photocatalytic micro-channel reactor was designed by exploiting porous ceramic disks as a support for TiO_2 photocatalyst. Ethanol solution of titanyl(IV)acetylacetonate and a commercial titania sol were used as the starting materials for the synthesis of TiO_2 layer. A rougher surface of the TiO_2 channel was prepared from titanyl(IV)acetylacetonate solution by comparing with that from a titania sol. Photocatalytic activity of the micro-channel reactor at various circulation velocities was evaluated by measuring the decay of absrobance of methylene blue aqueous solution. Since the porous disks prepared with the titania sol showed a higher photocatalytic activity at medium flow rates, the surface roughness of the TiO_2 was found to decrease the activity. A stagnation region near the rough surface may expand at higher flow rates and then the mass transfer between the TiO_2 surface and the laminar flow was suppressed for the reactant molecules and decomposition intermediates.

Keywords: Photocatalyst; Microreactor; Channel reactor; Porous ceramics; TiO_2; Methylene blue

1. Introduction

With the properties of being a photocatalyst, many attempts of researches and developments on titanium dioxide have been made to achieve the higher efficiency and advantageous applications. The research on the application to the wastewater treatment is very attracting and draws attention with many literatures released in the past few years. The photochemical technology using TiO_2 photocatalyst for the water treatment process is known as a clean method, because the substance is non-toxic and the undesirable by-products cannot be formed [1].

Chemical reactors can be classified into many systems such as batch reactor, batch recirculation reactor, and plug flow reactor [2]. However, designing any reactor models with reliable kinetic analysis is still complex and difficult. Especially, when the designed reactor is introduced to real working sites and used with the real wastewater, there are many variable parameters such as the concentration of reactant, and the unknown substances [3,4]. Furthermore, in photocatalytic reactors, since light is concerned in the reaction process, designing becomes more complicated and difficult task. The study for the micro-scale structure of photocatalyst make possible to control the fundamental properties and parameters of the system. The application from this study should be useful for more understanding in the design of photocatalytic micro-reactor and lead the future applications to micro-technology.

In this study, we have designed and evaluated a photocatalytic micro-channel reactor. Porous alumina ceramic disks were exploited as the support for titanium dioxide coating, and the design of reaction site in this micro-reactor was examined. Titanium dioxide was synthesized on the inner surface of these porous ceramic disks by pyrolysis method using two types of starting solution, and the characteristics of the TiO_2-coated disks were investigated. Methylene blue (MB) was used as the reactant because of the convenience in measuring concentration of solution. The photocatalytic activity was evaluated at several flow rates and under oxygen gas supplement.

2. Concept and design of photocatalytic micro-reactor

The applications in the field of photochemical engineering are settled by three factors; the optimization of the alignment for radiation sources, the reacting system, and the principles of chemical engineering. The design for an effective photo-

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catalytic micro-reactor can also be obtained by an appropriate arrangement of above-mentioned three aspects, which may be considered in details as [5]:

- The photocatalyst surface should be irradiated sufficiently to achieve the excitation of photocatalyst used in the system.
- The reactor geometry for the reactants must be chosen for the suitable dimensions and shapes, to achieve the contact of the reactant to the surface of the photocatalyst.
- Oxygen gas should be supplied at the reaction site.
- The flow rate or reaction time of the contaminated solution in the system should be optimized.

Different from the other well-known chemical reactors, photocatalytic micro-channel reactor was designed in the way of scaling down. Since the catalyst fixed to solid–liquid interface, the channel diameter should be in the range from 1 to 100 μm. However, by the fact that the special characteristic of photocatalytic reaction is the utilization of absorbed light to activating the reaction processes, equal distribution of radiation becomes important issues in designing the micro-scale channel reactor. Since the size of reactor channels is very small, the radiation source is unable to place inside the reactor as in the case of typical photoreactors. Then the radiation source has to be positioned outside the reactor and irradiates into the channels. In the case of micro-reactor, the angle of incident light becomes a special parameter. In our previous study, the optimal angle of light direction was found to be parallel to the central axis of the channel and making a slight angle to the channel axis decreased the photocatalytic activity [6].

3. Experimental

As the supports for TiO_2 photocatalyst, the porous alumina ceramic disks (Pilot Precision Co., Ltd.; diameter 5.0 mm, thickness 0.2 mm, containing 1250 channels of 50 μm diameter in 3.0 mm circle) were used. Fig. 1 shows the SEM images of the porous ceramic disk. For the synthesis of photocatalytic micro-reactor, titanyl(IV)acetylacetonate (TA, $(C_5H_7O_2)_2TiO$, Kanto chemicals Co., Inc.) and polyvinylpyrrolidone (PVP, $(C_6H_9NO)_n$, MW = 40,000, Tokyo Kasei Kogyo Co., Ltd.) were dissolved in ethanol at the weight ratio of TA:PVP = 1:2. Then the TA/PVP solution was diluted by ethanol to make the concentration of 20 wt.%. After well stirring at 60–70 °C, the solution was kept at room temperature for 24 h in order to obtain a homogeneous mixture. The surface of channels of porous ceramic disk was coated with thus obtained TA/PVP mixture by dipping, and then calcined in the following conditions. This coating process was repeated three times. In the first and second coating, the disk was calcined at 450 °C for 1 h, and in the third coating, it was calcined at 500 °C for 12 h. The formation of TiO_2 anatase phase after the calcination of TA at 500 °C has been confirmed in our previous study [7]. For comparison, another TiO_2 starting material, commercial grade titania sol (Mitsubishi Gas Chemical), was used in place of TA/PVP solution without further chemical adjustment.

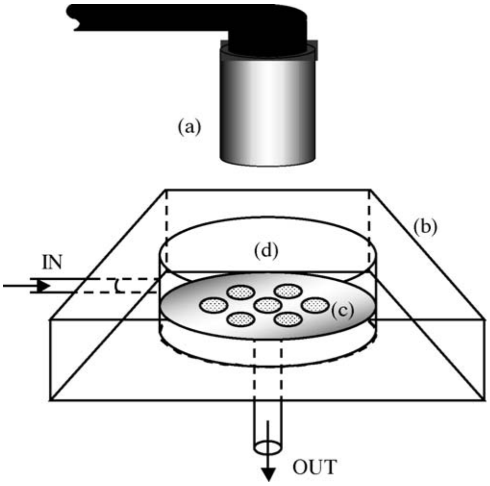

Fig. 2. The cell for photocatalytic evaluation: (a) UV light guide; (b) acrylic housing; (c) seven TiO_2-coated porous alumina disks; (d) cell chamber.

The photocatalytic micro-reactor was evaluated by measuring the decrease in the absorbance of MB solution with the time of UV irradiation. The MB solution was circulated through TiO_2-coated porous ceramic disks in an acrylic cell chamber as shown in Fig. 2. In the cell chamber, seven porous disks were mounted using a pair of plastic sheets, which have seven 3 mm ϕ holes to let MB solution flow through 1250 channels in each disk. The surface area of the top of the disk is calculated to be

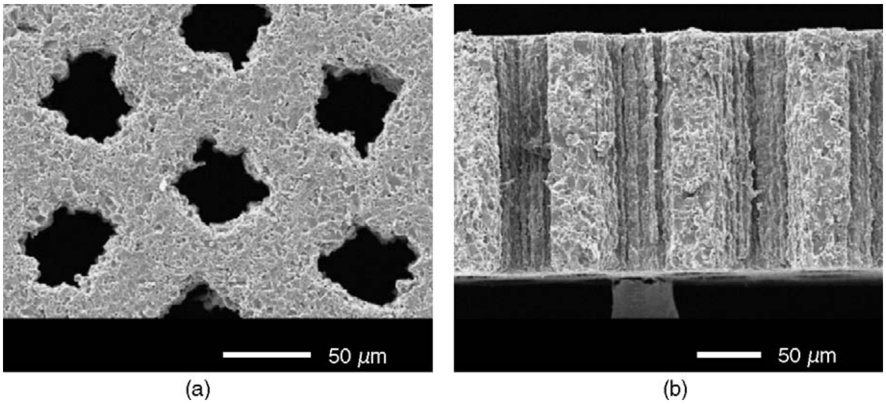

Fig. 1. SEM images of porous alumina ceramic disk: (a) lop view; (b) cross-sectional view.

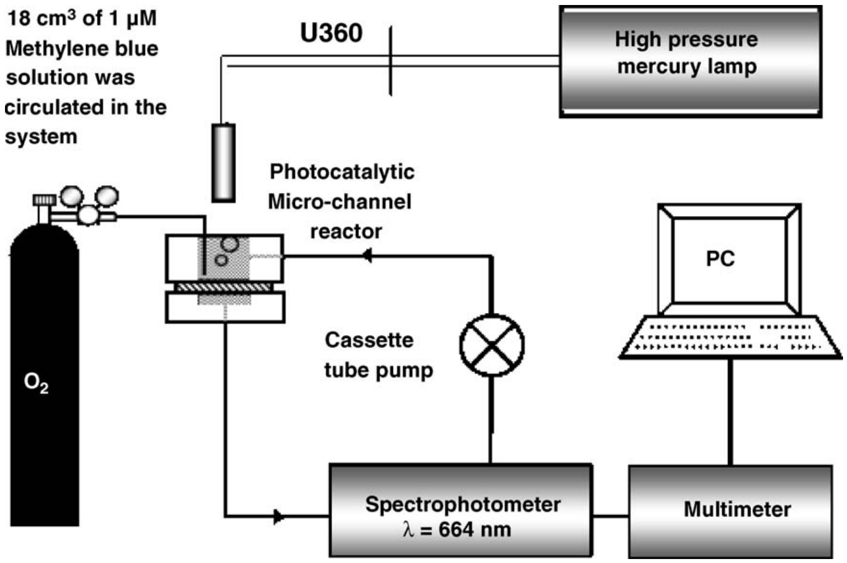

Fig. 3. Schematic illustration for the experimental set-up to evaluate the photocatalytic activity of the channel reactor.

4.6 mm^2, while the total surface area of 1250 channels in one disk is about 20 mm^2. Since the cross-section of channel is not circle as shown in Fig. 1, the area of inner surface may be larger than this value. Then from the geometrical estimation, we concluded that the reaction takes place mainly at the inner surface of the channels.

Fig. 3 shows the schematic illustration of experimental set-up for the evaluation of photocatalytic activity of the micro-channel reactor. Through the micro-reactor and an optical cell mounted in a spectrophotometer (HITACHI, U-3210), 18 cm^3 of 1 μM MB solution was circulated by means of a cassette tube pump (EYELA, SMP-23S). The micro-reactor was irradiated by a 250 W high-pressure mercury lamp (USHIO DENKI, SX-UI251HQ) through a UV light guide with a band pass filter (HOYA, U360). The light energy density was measured to be 2.0 mW cm^{-2}. Before starting the irradiation, MB solution was circulated in the dark condition for 12 h to achieve the steady-state condition for MB adsorption in the system. The absorbance of MB solution was continuously measured at 664 nm. The signal from the spectrophotometer was collected automatically by a personal computer using the Exlogger program at a fixed interval of time through a multimeter (HEWLETT PACKARD, 34401A). Eight flow rates ranging from 1.3 to 11.4 cm^3 min^{-1} were used to circulate MB solution.

The top side of the acrylic reactor was designed to open to the air for the sake of dissolution of oxygen into the solution. We investigated the effect of oxygen on the efficiency of the photocatalytic reaction by running the experiments with the supplement of oxygen gas from a cylinder. In this case, oxygen gas was supplied at the rate of 3.4 cm^3 min^{-1} by bubbling to allow molecular oxygen in the reactor to be saturated.

4. Results and discussion

Fig. 4 shows the SEM images of TiO_2 layers synthesized from TA/PVP solution and titania sol. The surface of TiO_2 layers is not flat because the original characteristic of porous ceramic as shown in Fig. 1. The thickness of TiO_2 layers was about 2 μm by estimating from the cracked section. Although the thicknesses for both coating methods were nearly the same, we could notice that the characteristic of the surface was different to each other. The TiO_2 layer on the channel wall synthesized from TA/PVP system has a rougher surface than that prepared from the titania sol. The higher roughness means the higher surface area that

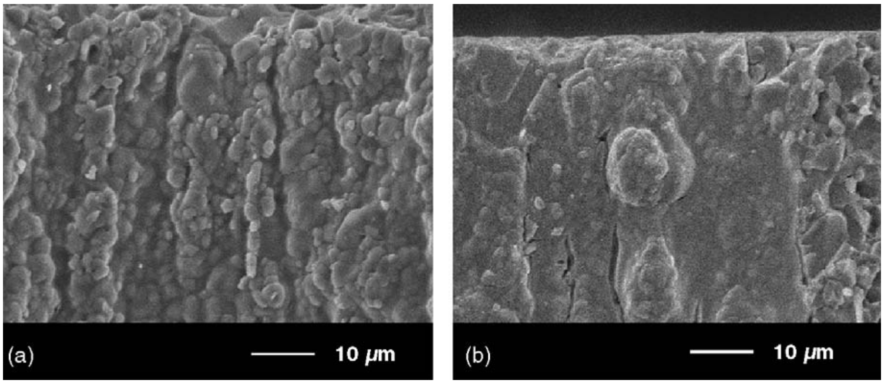

Fig. 4. SEM images of TiO_2-coated porous ceramic disk prepared from: (a) TA/FVP solution; (b) titania sol.

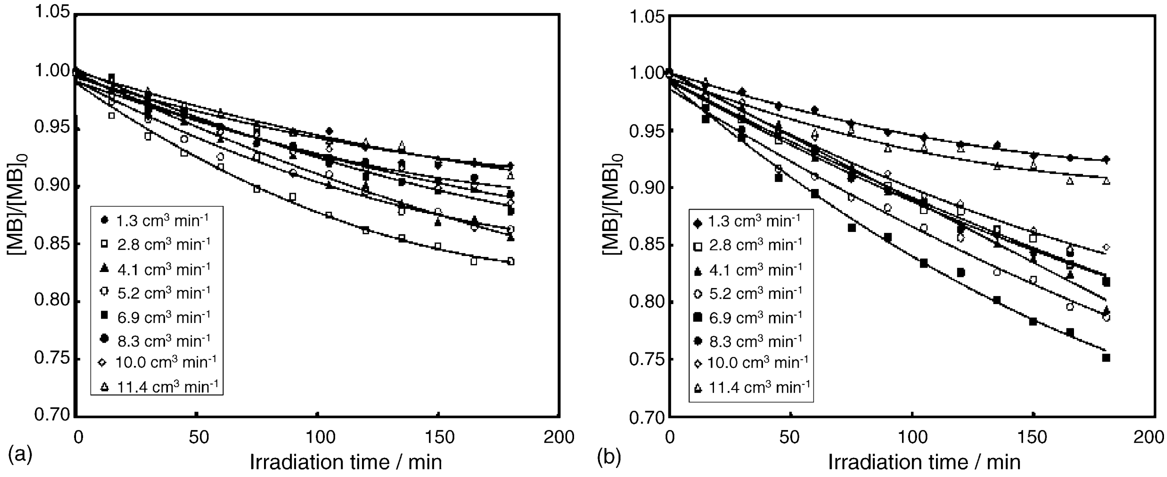

Fig. 5. Decay of the MB concentration at various flow rates by the photocatalytic reaction with TiO_2 channel reactor prepared from TA/PVP: (a) in the air; (b) with oxygen gas supplement.

is likely advantageous for photocatalytic activity. Although the difference in the surface area of porous ceramics could not be measured precisely by the BET method owing to an insufficiency of the total surface area, the present experimental result of flow rate dependence could be discussed, irrespective of the surface area.

Fig. 5 shows the evaluation of photocatalytic activity for the micro-channel reactor prepared with TA/PVP solution. The evaluation condition in Fig. 5(a) was in the air while that in Fig. 5(b) was under oxygen gas bubbling. The observed change in the concentration could be analyzed with the pseudo-first-order kinetics. From the semi-logarithmic plot, the apparent rate constant, k, was evaluated as the slope [6].

Fig. 6 shows the tendency of the reaction rate (k) at the various flow rates of MB solution. The values of k increased at a low flow rate and then decreased with increasing the flow rate. By supplying oxygen gas to the reactor, the reaction rate k increased, because molecular oxygen takes an important role in the photocatalytic decomposition of organic molecules. The slight increase of k up to a medium flow rate indicates that the reaction rate is determined by mass transfer, which is increased by the elevating flow rate.

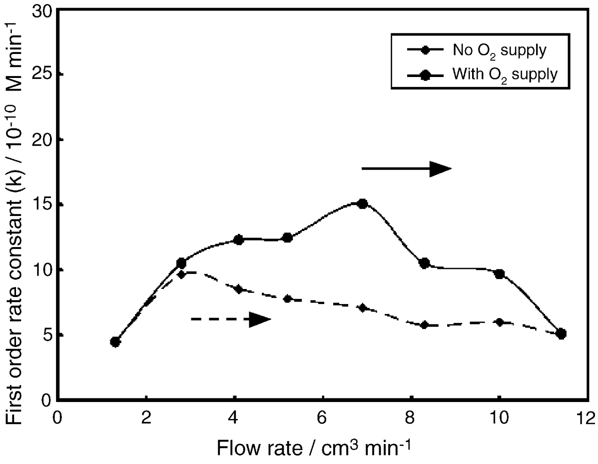

Fig. 6. Effect of flow rate of the MB solution on the first order rate constant (k) of the photocatalytic micro-channel reactor prepared from TA/PVP solution. Arrows show the flow rate at which stagnation become significant.

Fig. 7 shows the evaluation of photocatalytic activity under air (a) and oxygen gas supplying (b) for the micro-channel reactor prepared with titania sol. This result also shows the similar tendency to that for the TA/PVP system. The reaction rate k was calculated from the data in Fig. 7 and plotted in Fig. 8 as a function of the flow rate. At the flow rate of 1.3 $cm^3\ min^{-1}$ with oxygen supply, the value of k for titania sol was the same as that for TA/PVP. Since the effect of flow is small at this smallest flow rate, the photocatalytic activity of rough TiO_2 surface is similar to that of smoother TiO_2 surface. The difference in the characteristics of the TiO_2 appeared as the effect of flow rate as shown in Figs. 6 and 8.

In order to understand the effect of flow rate, the flow velocity of MB solution in the micro-reactor channels was calculated. The chamber, (d) in Fig. 2, was considered as a control volume with inlet and outlet. From the principle of conservation of mass [8], since the total mass of MB solution in the reactor chamber (M_{chamber}) is not changed with time, mass flow rate of MB solution at input ($\dot{m}_{\text{in}}$) is equal to that at output ($\dot{m}_{\text{out}}$)

$$\frac{dM_{\text{chamber}}}{dt} = \dot{m}_{\text{in}} - \dot{m}_{\text{out}} = 0 \tag{1}$$

And from the relation that

$$\dot{m} = \rho A \bar{u} \tag{2}$$

$$\rho A_{\text{in}} \bar{u}_{\text{in}} = \rho A_{\text{channel}} \bar{u}_{\text{channel}} \tag{3}$$

where ρ is the density of MB solution, A_{in} the cross-sectional area of the reactor inlet, $\bar{u}_{\text{in}}$ the averaged inlet velocity, A_{channel} the total of the cross-section at the reactor channel, and $\bar{u}_{\text{channel}}$ is the average velocity in the channel. The velocity of MB solution in one channel can be calculated from the flow rate by applying the above relationship. From the averaged flow velocity the Reynolds number (Re) can be calculated by means of Eq. (4) on

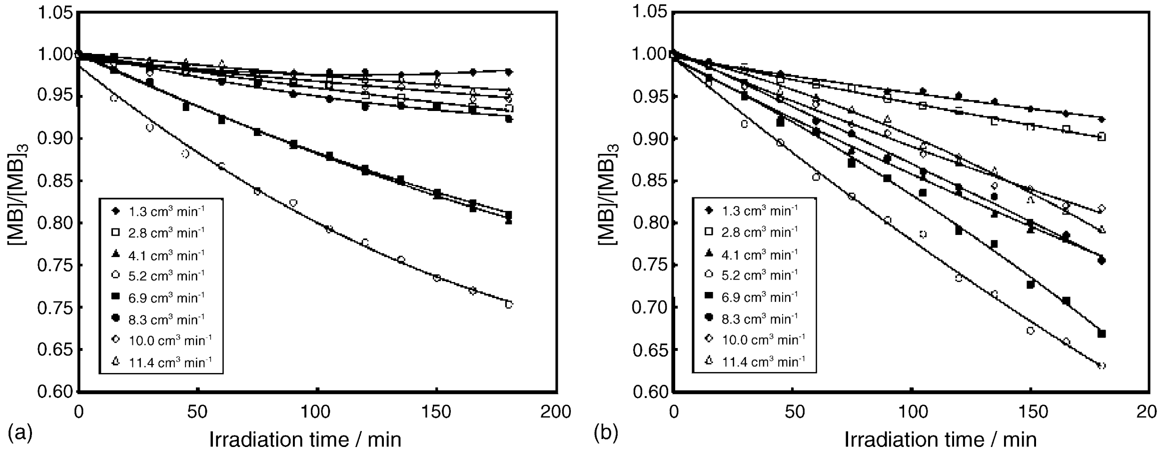

Fig. 7. Decay of the MB concentration at various flow rate by the photocatalytic reaction with TiO_2 channel reactor prepared from titania sol: (a) in the air; (b) with oxygen gas supplement.

the assumption of cylindrical channels.

$$Re = \frac{\rho \bar{u}_{\text{channel}} D}{\mu} \tag{4}$$

where D is the diameter of the channel (50 μm), μ the viscosity of the solution (0.001 Pa s). In Table 1 listed are the flow velocity and the Reynolds number at the various flow rates.

Since the Reynolds numbers are smaller than the critical Reynolds number, 2.3×10^3, the flow condition inside the micro-reactor channels is indicated to be laminar flow. As the surface of TiO_2 layer was rough, however, the flow condition inside the channels could not be a perfect laminar across the channel.

The condition of “stagnation” could occur at the uneven surface of the channels as illustrated in Fig. 9. Since the stagnating condition will not occur prominently at the low flow rate, the decomposed MB molecules could easily diffuse to the laminar flow in the channel, and being circulated in the evaluation system. When the flow rate was increased up to a certain value, which depends upon the profile of wall surface, the reaction rate increased because the lateral mass transfer by diffusion from the channel wall to the laminar flow region increases with the flow rate. When the flow rate increased above the critical value, the stagnation becomes likely significant. Since the stagnation layer separate the TiO_2 channel wall from laminar flow region, the reactant MB molecules in the flow are trapped at the stagnating layer before they transfer to the TiO_2 surface to be decomposed photocatalytically. Then the lateral mass-transfer across the stagnation layer takes time to slower the photocatalytic reaction. Consequently, the reaction rate in the micro-channel reactor was decreased at the higher flow rates as observed in Figs. 6 and 8.

Table 1
Flow velocity of MB solution in the micro-reactor channels ($\bar{u}_{\text{channel}}$) and Reynolds number (*Re*)

Flow rate (cm^3 min^-)	$\bar{u}_{\text{channel}}$ (10^{-3} m s^{-1})	Reynolds number (*Re*)
1.3	1.26	0.063
2.8	2.72	0.136
4.1	3.98	0.199
5.2	5.06	0.253
6.9	6.70	0.335
8.3	8.06	0.403
10.0	9.70	0.485
11.4	11.08	0.554

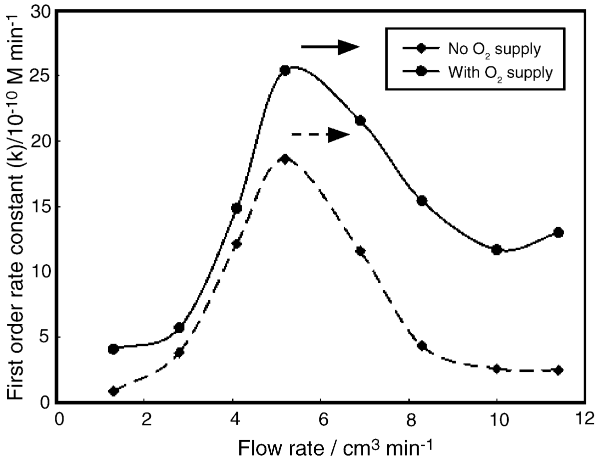

Fig. 8. Effect of flow rate of the MB solution on the first order rate constant (*k*) of the photocatalytic micro-channel reactor prepared from titania sol. Arrows show the flow rate at which stagnation become significant.

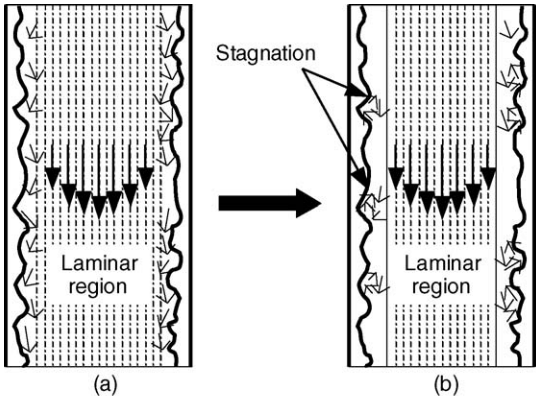

Fig. 9. Illustration for the formation of stagnating condition in the channel of photocatalytic micro-reactor: (a) low flow rate; (b) high flow rate.

Usually, a larger surface area shall be an advantage in using the photocatalyst. We supposed that the micro-channel reactor prepared from TA/PVP that has the rougher surface should show a higher efficiency in MB decomposition. However, the present experimental data showed that the reaction rate at a slowest flow shows similar values, indicating the difference in the surface area does not affect the reaction rate. The effect of the surface roughness appeared to change the reaction rate in the flow rate dependence. The smoother surface provides a higher reaction rate at a medium flow rate in this experiment. Since in the faster flow region the reaction rate decreased for all cases, the primary factor that affected the kinetics in the flow reactor should be the stagnation.

Though in the present study, decoloration of MB molecules was employed to test the photocatalytic reaction rate, the actual pollutant should be decomposed completely. For complete decomposition, the stagnation of flow at TiO_2 surface is likely favorable. Then for further evaluation of the flow reactor, the analysis of product such as CO_2 is also desirable.

5. Conclusions

The TiO_2 layer was synthesized on the channel surface of porous ceramic disks by pyrolysis method using two different starting solutions. The micro-reactor prepared from titania sol showed the higher photocatalytic activity than that prepared from TA/PVP solution at almost all flow rates. We found that the roughness of the reactor channel affected the photocatalytic activity because the stagnation region formed at TiO_2 surface retards the mass transfer from the channel wall to the laminar region of the channel flow. Designing of the photocatalytic flow micro-reactors should take the surface profile into account because the stagnation becomes an important factor for mass transfer. The present results indicate that the smother the channel surface becomes, the more efficient photocatalytic reaction can take place at a higher flow rate.

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